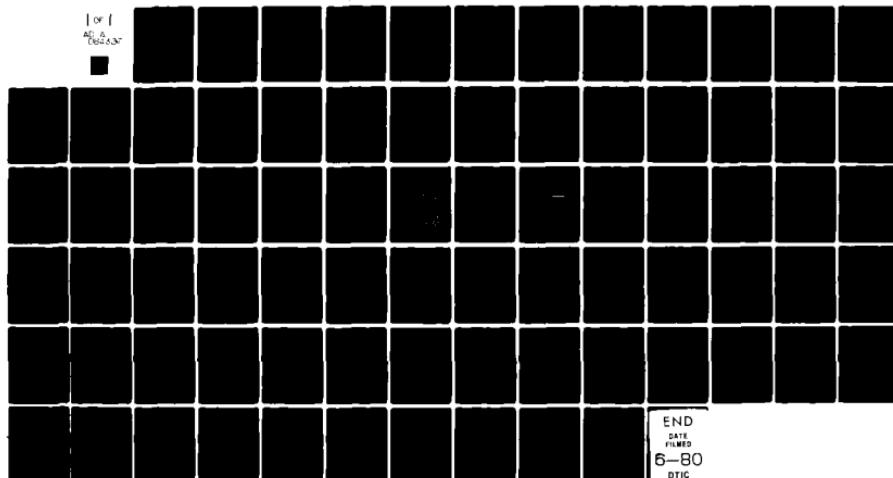


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Chelating Alkenyl Phosphine Ligands.

By

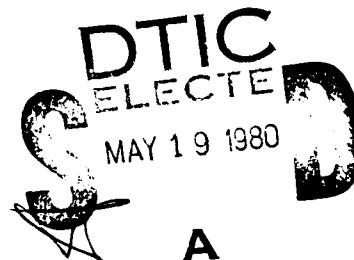
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Closo and Hyper-Ccloso Ten-Vertex Ruthenacarboranes Containing
Chelating Alkenyl Phosphine Ligands

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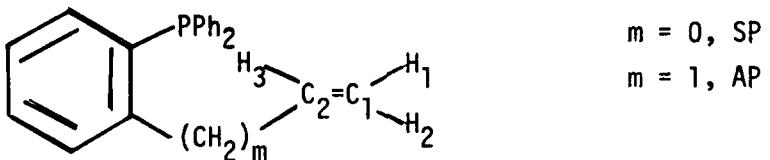
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ABSTRACT

Reactions of [hyper-closo-2-R¹-3-R²-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₇](I) with (*o*-styryl)diphenylphosphine (R^{1,2}=H,CH₃; R¹=H,R²=Ph), (*o*-allylphenyl)diphenylphosphine(R^{1,2}=H,CH₃) and Ph_{3-n}P(CH₂CH₂CH=CH₂)_n(n=1,2; R^{1,2}=CH₃) afforded the 16e⁻ ruthenacarborane complexes [hyper-closo-RuL(C₂B₇H₇R¹R²)] (IIa-g), in which the alkenyl phosphine (L) functions as a bidentate ligand. The crystal structure of [2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇](IID) was determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group P2₁/c with a=11.740(3) Å, b=15.185(5) Å, c=21.748(7) Å, β=137.43(2)⁰ and Z=4. Refinement of 4168 independent reflections with I>3σ(I) led to a final value of R=4.0%. The structure of this complex may best be described in terms of a C₂B₇ fragment of arachno-geometry which occupies nine vertices of an eleven-vertex octadecahedron with a ruthenium atom in a "non-vertex" position and within bonding distance of six atoms in the open face. The observed distortion from the common ten-vertex bicapped square antiprismatic structure is thought to be a result of the perturbation of the polyhedral skeletal bonding induced by the sixteen-electron Ru^{II} center. Reaction of (IIb) with carbon monoxide displaced the coordinated alkenyl side-chain to yield the 18e⁻ Ru^{II} complex [closo-6,6-(CO)₂-6-L-6,2,3-RuC₂B₇H₉](IIIa){L=(*o*-allylphenyl)-diphenylphosphine}.

Reactions of Ph_{3-n}P(CH₂CH₂CH=CH₂)_n(n=1,2) with [hyper-closo-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₉] produced the fluxional complexes [closo-6,6-L₂-6,2,3-RuC₂B₇H₉](IVa-b) which exhibit butenyl side-chain exchange and undergo closo-hyper-closo equilibria as evidenced by variable temperature multinuclear FTNMR spectroscopy. The reactions of (IVa-b) with carbon monoxide are also discussed.

As part of our study of metallocarborane-catalyzed homogeneous hydrogenation and isomerization of alkenes,^{1,2} we have attempted to isolate or detect possible intermediates in the catalytic cycle.³ Although we have previously noted that the unsaturated ruthenacarboranes $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_n\text{H}_{n+2})]$ ($n=7^4, 9^2$) react with electron-deficient alkenes we were unable to isolate alkene-metallocarborane complexes because of their instability. To overcome this difficulty, the potentially chelating alkenyl phosphines⁵ (o-styryl)-diphenylphosphine (SP),⁶ (o-allylphenyl)diphenylphosphine (AP)⁷ and $\text{Ph}_{3-n}\text{P}-$



$(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_n$ ($n=1$, but-3-enyldiphenylphosphine {MBP}; $n=2$, di(but-3-enyl)phenylphosphine {DBP})⁸ were used to prepare derivatives of the above ruthenacarboranes. This paper describes the synthesis and properties of such alkenyl phosphine complexes prepared from $[2-\text{R}^1-3-\text{R}^2-6,6-(\text{PPh}_3)-6,2,3-\text{RuC}_2\text{B}_7\text{H}_7]$ (Ia-c; $\text{R}^1,2=\text{H}$ or Me; $\text{R}^1=\text{H}$, $\text{R}^2=\text{Ph}$).

The complex $[2,3-(\text{CH}_3)_2-6-(\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P})-6,2,3-\text{RuC}_2\text{B}_7\text{H}_7]$ was the subject of a single crystal X-ray diffraction study, which revealed several interesting structural features. Unlike previously isolated metal complexes derived from the 1,3-dicarba-arachno-nonaborane(13) cage system,⁹ this complex has the metal within bonding distance of all six atoms in the open face. Distortion from the standard closo-structure was anticipated as this n-vertex polyhedron contains only $2n$ skeletal bonding electrons, as does $[\text{hyper-closo}-\{(\eta^5-\text{C}_5\text{H}_5)\text{Fe}\}_2-\text{C}_2\text{B}_6\text{H}_8].^{10}$

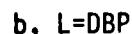
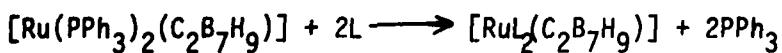
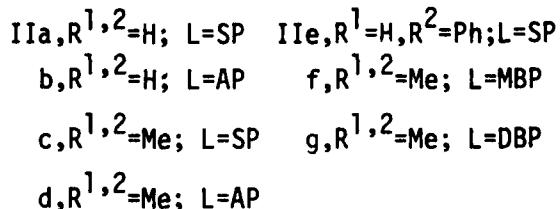
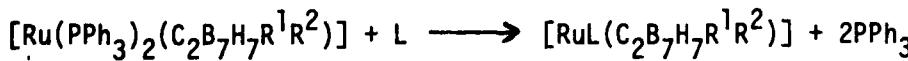
The complexes $[\text{closo-}6,6-\text{L}_2-6,2,3\text{-RuC}_2\text{B}_7\text{H}_9]$ ($\text{L}=\text{MBP}$ or DBP) were the subject of a variable temperature multinuclear FTNMR study which demonstrated the existence of two types of exchange processes. The first involves exchange of metal-coordinated and uncoordinated butenyl side-chains, while the second involves phosphine ligand dissociation with concomitant polyhedral rearrangement (closo-hyper-closo equilibrium).

RESULTS AND DISCUSSION

Synthesis, Reactivity and Spectral Data for Hyper-closo Ruthenacarboranes

The reactions of $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_7\text{R}^1\text{R}^2)]$ with SP or AP ($\text{R}^{1,2}=\text{H}$ or Me ; $\text{R}^1=\text{H}$, $\text{R}^2=\text{Ph}$ SP only) and MBP or DBP ($\text{R}^{1,2}=\text{Me}$) afforded the deep-red crystalline compounds $[\text{RuL}(\text{C}_2\text{B}_7\text{H}_7\text{R}^1\text{R}^2)]$ (IIa-g; L = alkenyl tertiary phosphine; See Table I). Elemental analyses and mass spectral data agreed with the proposed empirical formulae for IIa-g. Except for L=DBP(IIg), the infrared spectra of IIa-g contained no bands near 1630 cm^{-1} due to $\nu_{\text{C}=\text{C}}$ for a free alkene group. Instead, medium to weak bands at 1470 and 1260 cm^{-1} assignable to a coordinated alkene were observed.^{11,12}

TABLE I. Synthesis of Closo and Hyper-closo Ten-Vertex Ruthenacarborane Complexes



The NMR spectra of complexes IIa-g were also consistent with coordination of the alkene side-chain to the ruthenium atom. The alkenyl proton resonances were shifted 1.4 to 3.7 ppm upfield from the corresponding resonances of the free ligand. With ^{31}P -decoupling, the alkenyl proton resonances of $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_9)]$ (IIa) appeared as a first-order AMX spin system with no detectable geminal coupling between H_1 and H_2 (Figure 1). These alkenyl signals were assigned by assuming that the magnitudes of trans-

Figure 1

vicinal couplings (J_{2-3}) remain larger than the corresponding cis-couplings (J_{1-3}) upon complexation of the alkenyl group to ruthenium. The alkenyl coupling constants of IIa-g were smaller than those in the free ligands^{8,13,14} and similar to those found in other transition metal complexes containing chelating alkenyl phosphines or arsines.¹³⁻¹⁶ In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the alkenyl carbons of IIa-g appeared approximately 42 to 60 ppm upfield from those of the free phosphine.¹⁷ Off-resonance decoupled and proton-coupled spectra (for sufficiently soluble compounds) were used to assign these resonances.

The ^{11}B NMR spectra of compounds IIa-g were consistent with the presence of an asymmetric carboranyl ligand (see Figure 2). Those of IIIf-g

Figure 2

contained seven doublets ($J_{\text{B}-\text{H}} \approx 120$ Hz) of roughly equal areas and the spectra of IIa-e were similar, but not as well resolved. As in the parent, $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_7\text{R}^1\text{R}^2)]$,⁴ the complexes IIa-g exhibited resonances at about

107 ppm (relative to external $\text{BF}_3 \cdot \text{OEt}_2$) suggesting that the basic closed polyhedral ruthenacarborane structure was retained in the phosphine metathesis reaction. The ^1H NMR spectra of IIc-d showed two singlets due to two non-equivalent cage-methyl groups, while those of IIa-b contained only one carboranyl C-H singlet, the other carboranyl C-H signal presumably being obscured by the aromatic resonances in the 2.7-3.2 τ range. This notion is supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of IIb which exhibited two broad singlets (ca. 50 Hz halfwidths) at 106.3 and 122.2 ppm due to the two carboranyl carbon atoms. The other complexes either showed only one cage-carbon resonance (the second resonance is presumably buried under the aromatic carbon peaks), or were not sufficiently soluble to yield observable cage-carbon peaks. Cage-bonded methyl signals were not observed in the ^{13}C NMR spectra of IIc-d and may be too broad to detect at ambient temperature.^{18,19}

The spectral data presented for IIa-g are consistent with the alkenyl phosphines acting as bidentate ligands. Since complexes IIa-g are electronically and somewhat coordinatively unsaturated, the two alkenyl groups of the ligand di(but-3-enyl)phenylphosphine could conceivably coordinate to the ruthenium atom.²⁰ However, the infrared, ^1H and ^{13}C NMR spectra of IIg showed the presence of both free and coordinated butenyl side-chains. The ^1H NMR spectrum was essentially temperature-invariant over the range -50 to 40°C, ruling out an equilibrium between free and coordinated alkene.²¹ Steric hindrance and/or the additional metal-cage bonding interactions may prevent both butenyl side-chains from bonding to the ruthenium atom simultaneously.

Complexes IIa-g were air-stable in the solid state, but decomposed slowly in air-saturated solutions. They did not react with hydrogen (1 atm) or dry hydrogen chloride and complex IIa was an ineffective catalyst for alkene hydrogenation under mild conditions. No reduction of the alkenyl side-chain^{21,22} of IIa was discernible even after several days in benzene solution under 1 at-

mosphere pressure of hydrogen.

Treatment of IIb with carbon monoxide rapidly produced a yellow complex with empirical formula $[\text{Ru}(\text{CO})_2(\text{L})(\text{C}_2\text{B}_7\text{H}_9)]$ (IIIa; L=AP). The ^1H NMR spectrum of IIIa indicated that the allyl moiety is not coordinated to the metal atom. The carboranyl C-H resonances were not located, but the ^{11}B NMR spectrum of IIIa was almost identical to that of the complex $[\text{closo-6,6-(CO)}_2\text{-6-PPh}_3\text{-6,2,3-RuC}_2\text{B}_7\text{H}_9]$ ⁴ suggesting that the two Ru^{II} complexes are isostructural.

Complex IIIa and its PPh₃ analog are isoelectronic with $[\text{H}(\text{PPh}_3)_2\text{MC}_2\text{B}_7\text{H}_9]$ (M=Rh, Ir)⁴ and $[\{(n^5-\text{C}_5\text{H}_5)\text{Co}\}_2\text{C}_2\text{B}_6\text{H}_8]$,²³ and they presumably possess bicapped square antiprismatic structures, consistent with their formulation as saturated, ten-vertex closo polyhedra.²⁴ Complexes IIa-g and $[(\text{PPh}_3)_2\text{RuC}_2\text{B}_7\text{H}_9]$,⁴ however, are unsaturated complexes, all of which exhibit a low-field ^{11}B NMR resonance at about 105 ppm and are isoelectronic with $[\{(n^5-\text{C}_5\text{H}_5)\text{Fe}\}_2\text{C}_2\text{B}_6\text{H}_8]$, the structure of which has been determined.¹⁰ Nishimura has recently proposed²⁵ that the structure of $[\{(n^5-\text{C}_5\text{H}_5)\text{Fe}\}_2\text{C}_2\text{B}_6\text{H}_8]$ can be rationalized in terms of a "hyperpolyhedral" metal-metal bond between the two 17e⁻Fe^{III} centers of the cluster. In order to resolve this question by determining if an isoelectronic, unsaturated, monometallic ten-vertex cluster is, in fact, isostructural, an X-ray diffraction study of IIId was undertaken.

The Molecular Structure of [Hyper-closo-2,3-(CH₃)₂-6-(CH₂CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇], IIId.

Intramolecular distances and their estimated standard deviations are listed in Table VI. Average bond lengths are collected in Table VII. Bond angles and their associated estimated standard deviations are listed in Table VIII. The structure of [2,3-(CH₃)₂-6-(CH₂CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇] is shown in Figure 2, together with the numbering system employed.

The structure of this compound may be described in terms of a C₂B₇H₇Me₂ fragment of arachno geometry which occupies 9 vertices of an 11-vertex octadecahedron. The ruthenium atom occupies a position between the two empty vertices and is bound to the four boron atoms and two carbon atoms of the chair-shaped six-atom open face.

The ruthenium atom is thus bound to B(10), B(9), B(7), C(2), C(3), and B(1) of the carborane cage and to P, C(28) and C(29) of the (*o*-allylphenyl)diphenylphosphine ligand. The polyhedral carbon atoms occupy positions 2 and 3 in the fragment and are formally five coordinate. The structure of $[6,6-(\text{PPh}_3)_2-6,2,3-\text{RuC}_2\overset{\text{o}}{\text{B}}_7\text{H}_9]^4$ is probably similar with the ruthenium atom bonded to all six atoms in the open face (*vide infra*).

The ruthenium to cage distances can be compared to those in $[2,2-(\text{PPh}_3)_2-2,2-\text{H}_2-2,1,7-\text{RuC}_2\overset{\text{o}}{\text{B}}_9\text{H}_{11}]$ which range from $2.22(2)\text{ \AA}$ to $2.32(2)\text{ \AA}$ for the five atoms of the carborane open face.² However, in the title compound, Ru-B distances involve bonds to boron atoms of different coordination numbers; Ru to 6-coordinate boron B(7), B(9), and B(1) are $2.466(5)$, $2.340(5)$, and $2.488(5)\text{ \AA}^0$, respectively, and Ru to 5-coordinate B(10) is $2.023(5)\text{ \AA}^0$. A similar change in Fe-B bond lengths is noted in a compound with comparable cage geometry, $[\text{hyper-closo}-1,6-(n^5-\text{C}_5\text{H}_5)_2-1,6,2,3-\text{Fe}_2\text{C}_2\overset{\text{o}}{\text{B}}_6\text{H}_8]$.¹⁰

As expected, the polyhedral carbon atoms occupy nonadjacent positions in this compound; they occupy two of the three low-coordinate positions and are related by a noncrystallographic mirror plane through Ru, B(10), B(8) and B(1). Variations from mirror symmetry are within three standard deviations in related bond distances with the exception of B(1)-C(3) and B(1)-C(2), Ru(6)-C(2) and Ru(6)-C(3), and Ru(6)-B(7) and Ru(6)-B(9). Two of these exceptions can be explained by *trans*-influence.²⁶ The phosphorous atom is *trans*- to B(9) and C(28)=C(29) is *trans*-to C(3). Ru-C(3) is significantly longer than Ru-C(2) and Ru-B(9) is significantly shorter than Ru-B(7).

Unlike $[1,6-(n^5-\text{C}_5\text{H}_5)_2-1,6,2,3-\text{Fe}_2\text{C}_2\overset{\text{o}}{\text{B}}_6\text{H}_8]$, boron-boron distances and carbon-boron distances within the polyhedron do not reflect the coordination of the various atoms; the shortest boron-boron distance, B(4)-B(5)= 1.743 \AA^0 , is between two 6-coordinate boron atoms, and the longest distances, B(1)-B(4), B(1)-B(5) and B(8)-B(9), 1.814, 1.820, and 1.814 \AA^0 , respectively, are also between two 6-coordinate boron atoms.

In general, the bond lengths and angles within the $\text{C}_2\overset{\text{o}}{\text{B}}_7$ fragment correlate well with the analogous bonds in $\text{arachno-C}_2\overset{\text{o}}{\text{B}}_7\text{H}_{11}\text{Me}_2$.²⁷ The largest deviation is found for B(7)-C(3) and B(9)-C(2). The corresponding distances in the *arachno* compound are 0.13 \AA^0 longer than those in the metallocarborane.

B(9), C(3), P, and the midpoint of C(28)=C(29) are in a square planar conformation about Ru and C(28)=C(29) is nearly perpendicular to this plane. The Ru-P distance of 2.418(1) Å is within the range of distances found for ruthenium bonded to phosphines, but is longer than those found in [2,2-(PPh₃)₂-2,2-(H₂)-2,1,7-RuC₂B₉H₁₁] (2.342(4) and 2.301(4) Å).² The longer bond in the title compound may be due to the bulky phosphine ligand with its allyl group. The Ru-C distances of 2.167(4) and 2.191(4) Å are well within the range of distances for Ru π-bonded to an alkene.

Angles and distances involving the phosphorus atom are unexceptional. Although the phenyl ring of the o-allylphenyl moiety is planar, the dihedral angle C(27)-C(26)-C(21)-P is 4.4° and C(27), C(28), H(28), C(29), H(291) and H(292) are not coplanar. The linkage C(27)-C(28) is a normal single bond (1.5306(6) Å) and the distance C(28)-C(29) (1.406(7) Å) is within the range for π-bonded C=C distances. The distance of 1.498(6) Å for C(26)-C(27) and distances and angles in the phenyl ring are not unusual.

The only intermolecular distance less than 2.5 Å is between H(292) and H(513) and is 2.44 Å. Only two nonhydrogen-hydrogen intermolecular distances are less than 3.0 Å and they are between phenyl carbon atoms and a phenyl hydrogen atom and a methyl hydrogen atom, respectively; each distance is 2.96 Å.

The polyhedral geometry of the title compound is significantly different from the bicapped square antiprism found for ten-vertex clos-borane species such as (B₁₀H₁₀)²⁻²⁸ and [(C₅H₅)₂Co₂C₂B₆H₈]²³ but is very similar to [(C₅H₅)₂Fe₂C₂B₆H₈]¹⁰ and does adopt a fully triangulated closed polyhedral structure. If the title compound was constrained to have the bicapped square antiprism form, a new bond would be needed between C(2) and C(3) and the Ru-B(1) bond would be broken. Then B(1) would be in a lower coordinate position and C(2) and C(3) would be located in 6-coordinate positions.

The structures of the two hyper-closo ten-vertex metallocarboranes mentioned above also do not correspond to the predicted capping of the closo nine-vertex tricapped trigonal prism²⁹⁻³¹ but are instead a result of completely capping the six-membered open-face of the arachno C₂B₇ fragment, presumably to compensate for the electronic unsaturation of the metal center.

Synthesis, Reactivity and Variable Temperature Multinuclear FTNMR Studies of
Closo-Ruthenacarboranes

Complex [6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₉](Ia) reacted with MBP and DBP to produce yellow complexes with empirical formulae [RuL₂C₂B₇H₉] (IVa-b; L=MBP and DBP, respectively). The infrared spectra of IVa-b in the solid state contained both free and coordinated butenyl absorptions.¹² Solutions of IVa in toluene or dichloromethane were red at or above room temperature and the solution infrared spectrum in dichloromethane at 22°C exhibited two additional peaks assignable to a coordinated butenyl side-chain at 1325 and 1285 cm⁻¹ along with those at 1630(free), 1300 and 1250 cm⁻¹(coordinated) observed in the solid state spectrum.³⁵

Complex IVb did not yield red solutions until the temperature was above about 60°C. As the ligand cone angle³⁶ of MBP (140°) is larger than that of DBP (135°) it was presumed that phosphine ligand dissociation occurs to yield the unsaturated, red [hyper-closo-LRuC₂B₇H₉] species. This proposal was supported by the observation of a low-field ¹¹B NMR resonance at 107.5 ppm in a d₂-dichloromethane solution of IVa at 44°C, which was absent at -40°C. In addition, while treatment of IVb with carbon monoxide yielded [closo-(CO)L₂RuC₂B₇H₉] in high yield, the yield of the analogous monocarbonyl complex of IVa decreased with increasing temperature due to the formation of the dicarbonyl complex [closo-(CO)₂L₂RuC₂B₇H₉] (vide infra).

The variable temperature ³¹P{¹H} FTNMR spectrum of IVa in dichloromethane shown in Figure 3 indicated that the [closo-L₂RuC₂B₇H₉] species which predominates

Figure 3

at low temperatures is itself fluxional. At -73°C the spectrum consisted of a doublet for the chelated alkenyl phosphine ligand^{12,37} at 68.5 ppm ($^{23}\text{P}_{\text{P-P}} = 32$ Hz) and a doublet for the unidentate phosphine ligand at 47.2 ppm. As the temperature was raised, these resonances broadened, but before coalescence was attained, phosphine dissociation started to occur, as evidenced by the change in chemical shift of the unidentate phosphine ligand towards the free ligand limit. The spectrum at 60°C in 10% $\text{C}_6\text{D}_6-\text{C}_6\text{H}_5\text{CH}_3$ represented the high-temperature limit and exhibited a singlet at 49.8 ppm for the [hyper-closo-L $\text{RuC}_2\text{B}_7\text{H}_9$] species and a singlet at 45 ppm for the free alkenyl phosphine ligand.⁸ The presence of two exchange processes was more evident in the variable temperature $^{31}\text{P}\{^1\text{H}\}$ -FTNMR spectra of IVb in dichloromethane, as the temperature domains for the two processes were not overlapping. Thus, at -8°C , coalescence of the two inequivalent phosphorus nuclei occurred cleanly and the change in chemical shift of the unidentate phosphine ligand did not begin until above 27°C . (Figure 4)

Figure 4

The variable temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra of IVa were also complicated due to the overlap of the temperature domains of the two dynamic processes. At -78°C the $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectrum in dichloromethane exhibited free alkenyl carbons at 138.4 and 115.3 ppm, coordinated alkenyl carbons at 79.3 and 58.5 ppm and carboranyl carbons at 72.7 and 41.2 ppm.³⁸ Broad, free alkenyl carbon resonances were observed at -23°C and at 27°C the only resonances observed were due to exchange-averaged phenyl and methylene carbons of the alkenyl phosphine ligand. The ^1H FTNMR spectrum of IVa in d_2 -dichloromethane at -68°C consisted of three broad resonances at 5.39, 5.78 and 6.11 τ , in addition to three resonances at 4.34, 5.09 and 5.16 τ which can be assigned to the coordinated and free alkenyl protons of

butenyl side-chains, respectively.¹⁶ At -38°C these signals broadened and at 33°C only one set of three alkenyl protons was observed, suggesting that the low temperature exchange process is due to exchange of free and coordinated butenyl side-chains,²¹ as depicted in Figure 5.

Figure 5

The variable temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra of IVb in dichloromethane were more informative, although the presence of three inequivalent butenyl side-chains at the low temperature limit led to overlapping resonances and precluded complete spectral assignments. The $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra are shown in Figure 6.

Figure 6

At -83°C three sets of alkenyl carbons were observed at 142.3 and 119.2 (C_2' and C_1'), 138.5 and 115.6 (C_2 and C_1) and 74.8 and 52.5 (coordinated C_2 and C_1), where the primed carbons refer to those butenyl side-chains attached to the chelating phosphine ligand. The carboranyl carbons were observed at 75.9 and 39.2 ppm.³⁸ At -23°C only the C_1 and C_2 alkenyl carbon resonances were observed and at 27°C, again, only the exchange-averaged phenyl and methylene carbon resonances of the alkenyl phosphine ligand were present. The ^1H FTNMR spectra of IVb in d_2 -dichloromethane are presented in Figure 7.

Figure 7

At 88°C two sets of three free alkenyl proton resonances were observed

at 4.41, 4.60(H_3 and H'_3), 5.15 and 5.31 τ (H_1, H_2, H'_1 and H'_2 , overlapping), in addition to three coordinated alkenyl proton resonances at 6.00, 6.39 and 6.68. At 7°C two overlapping sets of three alkenyl proton resonances were present, while at 22°C only three alkenyl proton resonances were observed. It appears, then, from the $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H FTNMR spectral data, that there are, in fact, two low temperature exchange processes occurring for IVb in solution. The first involves exchange of one butenyl side-chain on each phosphine ligand between free and metal-coordinated sites, yielding equivalent phosphine ligands, one set of alkenyl carbon resonances due to the two non-fluxional butenyl side-chains and two sets of alkenyl proton resonances due to the two non-fluxional butenyl side-chains and the two exchange-averaged butenyl side-chains. The second process involves exchange of all four butenyl side-chains, yielding equivalent phosphine ligands, one set of exchange-averaged alkenyl protons and no observed alkenyl carbon resonances. The activation energy (ΔG^\ddagger) for the exchange of the first two butenyl side-chains is easily obtained from the $^{31}\text{P}\{^1\text{H}\}$ FTNMR spectra and is found to be 10.0 ± 0.5 kcal/mol.³⁹ The second process may be due to the onset of rotation about the ruthenium-phosphorus bond which would interchange the two butenyl side-chains on each phosphine ligand, thus enabling all four butenyl side-chains to exchange between free and coordinated sites.

The $^{11}\text{B}\{^1\text{H}\}$ FTNMR of IVb in d_2 -dichloromethane at -71°C resembled that of IVa at -40°C and illustrated the asymmetry induced in the carborane ligand when the phosphine ligands become inequivalent.

Complexes IVa-b reacted with carbon monoxide to form the yellow complexes [closo-6-CO-6,6-L₂-6,2,3-RuC₂B₇H₉](IVa-b; L=MBP or DBP). The infrared spectra of IVa-b included ν_{CO} absorptions at 1932 and 1930 cm^{-1} and $\nu_{\text{C}=\text{C}}$ (uncoordinated) at 1628 and 1632 cm^{-1} , respectively. The ^1H NMR spectra in d_2 -dichloromethane contained alkenyl proton resonances due to uncoordinated butenyl side-chains and exhibited no temperature-dependent behavior.⁴⁰ The presence of a mirror-plane was

indicated by the $^{11}\text{B}\{\text{H}\}$ and $^{31}\text{P}\{\text{H}\}$ NMR spectral data suggesting that the carboranyl cage mirror plane bisects the P-Rh-P angle in a static structure or, alternatively, that the $\{\text{RhP}_2\text{CO}\}$ vertex is rapidly rotating about the five-membered face of the carboranyl ligand as has been proposed for [clos- $\{\text{P}(\text{C}_2\text{H}_5)_3\}_3\text{RuC}_2\text{B}_7\text{H}_9$] at -88°C .⁴

The carbonylation of IVa produced Va in quantitative yield when monitored by $^{31}\text{P}\{\text{H}\}$ FTNMR at -78°C . At temperatures above 25°C , however, the carbonylation of IVa produced two additional singlet resonances at -15.3 and 45.4 ppm which were assigned to free but-3-enyldiphenylphosphine and to [clos-6,6-(CO) $_2$ -L-6,2,3-RuC $_2\text{B}_7\text{H}_9$] (IIIb; L=MPB), respectively. The infrared spectrum of IIIb in the $2100-1900\text{ cm}^{-1}$ region was very similar to that of the analogous complex, IIIa.

Conclusions

Reactions of [hyper-clos-2-R 1 -3-R 2 -6,6-(PPPh $_3$) $_2$ -6,2,3-RuC $_2\text{B}_7\text{H}_7$](I) with SP(R $^1,2=\text{H,CH}_3$; R $^1=\text{H}$; R $^2=\text{Ph}$); AP(R $^1,2=\text{H,CH}_3$), MBP and DBP(R $^1,2=\text{CH}_3$) yielded the unsaturated ruthenacarborane complexes [hyper-clos-RuL(C $_2\text{B}_7\text{H}_7\text{R}^1\text{R}^2)](IIa-g)$, in which the alkenyl phosphine (L) functions as a bidentate ligand. The molecular structure of IIId(L=AP, R $^1,2=\text{CH}_3$) was determined by X-ray diffraction to be similar to that of $[(\eta^5-\text{C}_5\text{H}_5\text{Fe})_2\text{C}_2\text{B}_6\text{H}_8]^{10}$ and represents a new structural class of ten-vertex metallocarboranes containing ten skeletal electron pairs. The term "hyper-clos" has been adopted to describe this structural class of which $[(\eta^5-\text{C}_5\text{H}_5)_3\text{Co}_3\text{B}_4\text{H}_4]$,³¹ $[(\eta^5-\text{C}_5\text{H}_5)\text{CoFe}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8]$,⁴¹ and $[\text{EFe}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8]$,⁴¹ (E=Sn,Ge) are also members, in order to differentiate these species from undistorted, unsaturated metallocarboranes, in which the electronic unsaturation is presumably largely metal-based. Studies are now underway in this laboratory to isolate and determine the molecular structure of twelve and eleven-vertex hyper-clos metallocarboranes in order to elucidate the nature

of the polyhedral distortions induced by the unsaturated metal vertices.

Reactions of [hyper-closo-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₉] with MBP and DBP yielded the saturated ruthenacarborane complexes [creso-RuL₂(C₂B₇H₉)](IVa,b). A variable temperature multinuclear FTNMR study of IVa,b indicated that the complexes undergo butenyl side-chain exchange in solution at lower temperatures and undergo creso-hyper-creso equilibria with concomitant polyhedral rearrangement at higher temperatures. This facile rearrangement demonstrates the remarkable mobility of transition metal vertices in cluster complexes and the flexibility of carborane cages in accommodating both electronic and coordinative unsaturation in the transition metal vertex.

Several interesting metallocarboranes containing carboranyl cage-bonded alkenyl side-chains have recently been prepared in this laboratory and the chemistry of these catalytically active species is currently under investigation.⁴²

EXPERIMENTAL SECTION

Crystal Structure

Crystals of II^d suitable for X-ray studies were obtained as black needles from CH₂Cl₂/pentane. A preliminary examination of several crystals by means of oscillation and Weissenberg photographs showed them to have monoclinic symmetry and systematic absences 0k0, k = 2n + 1, and h0l, l = 2n + 1, space group P₂₁/c.⁴³ The specimen selected for data collection was bounded by {102}, {010}, {110} and {110}. Crystal dimensions normal to these faces were 0.20, 0.16, 0.19, and 0.075 mm, respectively. The crystal was mounted on a Syntex P_T autodiffractometer equipped with a scintillation counter and a graphite monochromator. Lattice parameters, determined by a least-squares fit of 15 accurately centered high-angle reflections, were a = 11.740(3) Å, b = 15.185(5) Å, c = 21.748(7) Å, and β = 137.43(2)^o. The density measured by flotation in aqueous potassium iodide

was $1.36(1) \text{ g cm}^{-3}$, in good agreement with the calculated density of 1.368 g cm^{-3} based on $Z = 4$.

Intensity measurements were made with Mo κ radiation scan rate of $2.0^{\circ}/\text{min}$ from 1.25° below the $K\alpha_1$ reflection to 1.25° above the $K\alpha_2$ reflection. The background was counted for one half of the scan time at each end of the scan range. Data were collected with a θ - 2θ scan technique to a limit of $2\theta = 55^{\circ}$. Three strong reflections were checked after each 97 intensity measurements and these showed only random variations consistent with their respective $\sigma(I)$ values. Of the 6052 unique reflections not excluded by the space group, 1884 for which $I < 3\sigma(I)$ were considered unobserved. The remaining 4168 reflections were used in the structure determination and refinement. All measured reflections were corrected for Lorentz and polarization effects and processed to give $|F_O|$ values as previously reported.⁴⁴ An absorption correction was applied ($\mu = 6.60$; maximum and minimum transmission factors were .9559 for $\overline{13}018$ and .9479 for $\overline{11}028$.

Determination and Refinement of the Structure

Trial positions for the ruthenium and phosphorus atoms were obtained from a three-dimensional Patterson summation. The other atoms, including hydrogen atoms, were located by means of difference Fourier maps. Refinement, without the contribution of hydrogen atoms to calculated structure factors, of positional and anisotropic thermal parameters of the ruthenium and phosphorus atoms and of positional and isotropic thermal parameters of all other nonhydrogen atoms, converged to a conventional R^{45} index of 5.5% and a weighted index, R_w , of 7.5%. For reasons of economy, the two C_6H_5 moieties were then constrained to be rigid groups⁴⁶ containing C_6 hexagons of $C-C = 1.39 \text{ \AA}^0$ and $C-H = 1.0 \text{ \AA}^0$. Maxima in the range of $0.5 \pm 0.2 \text{ e A}^{-3}$ at positions close to those calculated for the remaining hydrogen atoms were found on a difference Fourier map. The two methyl groups were also constrained to be rigid groups containing an sp^3 carbon atom and $C-H =$

1.0 Å. Positional and anisotropic thermal parameters of all nonhydrogen nongroup atoms, positional and isotropic thermal parameters of all carbon group atoms and positional parameters of all nongroup hydrogen atoms were refined. Isotropic thermal parameters for all hydrogen atoms were assigned as follows: for all non-group hydrogen atoms $B = 5.0$, for all phenyl group hydrogen atoms $B = 0.5$ plus the B value on the adjacent carbon atom, and for all methyl group hydrogen atoms $B = 1.0$ plus the B value on the adjacent carbon atom. The refinement converged at $R = 4.0\%$ and $R_w = 4.8\%$. In the final least-squares cycle, the largest shift in a positional or thermal parameter for a nonhydrogen atom was 0.4σ . The final "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ was 1.47. In this expression $N_o = 4168$, the number of observed reflections, and $N_v = 267$, the number of variable parameters. No maxima $> 0.75 \text{ e } \text{\AA}^{-3}$ were found on a final difference Fourier map.

The final positional and thermal parameters are listed in Tables I, II, and III. A listing of the root-mean-square amplitudes of vibration of the nonhydrogen nongroup atoms along the three principal axes of the vibrational ellipsoids, together with the corresponding B values, is given in Table IV.⁴⁷ A set of structure factors was calculated on the basis of the tabulated parameters and is available as Table V.⁴⁷ The atomic scattering factors were those given in Table 2.2A of ref. 48 and the real and imaginary components of anomalous dispersion from Table 2.3.1 of ref. 43 were applied to the scattering factors of ruthenium and phosphorus.

Synthesis of Metallocarboranes

Unless indicated otherwise, all operations were conducted under purified nitrogen or argon using standard inert atmosphere techniques.⁴⁹

Infrared spectra were determined as mineral oil mulls or KBr pellets on a Perkin-Elmer 421 dual-grating spectrometer. Proton NMR spectra were measured using Varian A60D and HA100D spectrometers. ^{13}C NMR spectra were recorded on

a Varian CFT-20 spectrometer. The 80.5 and 111.8 MHz ^{11}B FTNMR spectra were obtained with an instrument designed and constructed by Professor F. A. L. Anet of this department. All other FTNMR spectra were recorded on a Brüker WP-200 spectrometer equipped with a B-ST-100/700C variable temperature unit. ^{11}B and ^{31}P chemical shifts were referenced to external $\text{BF}_3\cdot\text{OEt}_2$ and D_3PO_4 , respectively, with positive values assigned to low-field shifts and all reported coupling constants are absolute values. All NMR solvents were vacuum distilled from P_4O_{10} into the NMR sample tube prior to sealing under vacuum ($< 5 \times 10^{-5}$ torr). Mass spectra were obtained on an Associated Electrical Industries MS-9 spectrometer.

Melting points were determined in open capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

The complex $[\text{hyper-closo-2-R}^1\text{-3-R}^2\text{-6,6-(PPh}_3)_2\text{-6,2,3-RuC}_2\text{B}_7\text{H}_7]$ was prepared by a previously described procedure.⁴ SP⁶, AP⁷, MBP⁸ and DBP⁸ were prepared by literature methods. Toluene, benzene and petroleum ether (30-60°C) were distilled from calcium hydride. Other solvents were reagent grade and deoxygenated with bubbling nitrogen or argon immediately before use. All other chemicals were reagent grade and used as supplied.

Preparation of [hyper-closo-6-(SP)-6,2,3-RuC₂B₇H₉](IIa)

A toluene (2 ml) solution of $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_9)]$ (0.101 g, 0.138 mmol) and SP (0.0875 g, 0.304 mmol) was stirred overnight at room temperature yielding a deep blood-red solution. Pentane (10 ml) was gently layered above the toluene solution and the mixture was cooled to -15°C for 3 d. The resulting red-brown crystals of $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_9)]$ (IIa) (0.049 g, 68%) were filtered off in air, washed with methanol and pentane and vacuum dried, m.p.: 193-197°C. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{B}_7\text{PRu}$: C, 53.04; H, 5.26; B, 15.19. Found: C, 53.10; H, 5.42; B, 15.36. ^1H NMR (100 MHz, CD_2Cl_2): 7.85 (dd{ $J_{13}=8.4$, $J_{\text{P}-\text{H}_1}=1.3$ Hz}, H_1),

7.20 ($d\{J_{23}=11.9$, $J_{P-H} < 0.5$ Hz}, H₂), 4.87 ($q\{J_{P-H} < 0.5$ Hz}, H₃), 3.96 τ (br,s, carborane C-H). ¹³C{¹H} NMR (20.5 MHz, 20% CD₂Cl₂/CH₂Cl₂): 66.25(s,C₁, $J_{C_1-H}=152.5$, 159.8 Hz), 92.55 (s,C₂, $J_{C_2-H}=158.8$ Hz), and 110.1 ppm(br,s, carborane C{W_{1/2} ≈ 50 Hz}). ¹¹B NMR (80.5 MHz, CD₂Cl₂): 106.8(1); 18.9(1); 5.59(1); -3.75, -4.55, -5.94 (3, overlapping peaks); -8.82 ppm(1).

Analogous [RuL(C₂B₇H₇R¹R²)] complexes were prepared similarly by reactions of [2-R¹-3-R²-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₇] with the appropriate alkenyl phosphine: [Ru(AP)(C₂B₇H₉)](IIb), AP (0.208 g, 0.685 mmol), [Ru(PPh₃)₂(C₂B₇H₉)] (0.251 g, 0.342 mmol), 85% yield, m.p.: 157-160°C. Anal. Calcd for C₂₃H₂₈B₇PRu: C, 53.94; H, 5.51; B, 14.78; P, 6.05; Ru, 19.73. Found: C, 53.79; H, 5.65; B, 14.93; P, 6.28; Ru, 19.53. ¹H NMR (100 MHz, CD₂Cl₂): 8.37 (dd{J₁₃=7.8, J_{P-H₁}=2.5 Hz}, H₁), 7.53 (dd{J₂₃=13.0, J_{P-H₂}≈1 Hz}, H₂), 5.53 (m,H₃), 6.13(m,CH₂), 4.88 τ (br,s, carborane C-H). ¹³C{¹H} NMR (20.5 MHz, 20% CD₂Cl₂/CH₂Cl₂): 66.52 (s,C₁); 88.66 (d{⁴J_{P-C₂}=5.0 Hz}, C₂); 39.54 (d{³J_{P-C}=14.0 Hz}, CH₂); 106.3 and 122.2 ppm(br,s, carborane C). ¹¹B NMR (80.5 MHz, CD₂Cl₂): 108.4(1), 15.0(1), 4.80(1), -5.18(1), 7.01(2), -10.3(1) ppm. [Ru(SP)(C₂B₇H₇Me₂)](IIc), SP (0.15 g, 0.52 mmol), [Ru-(PPh₃)₂(C₂B₇H₇Me₂)] (0.206 g, 0.270 mmol). Anal. Calcd for C₂₄H₃₀B₇PRu: C, 54.78; H, 5.75; P, 5.88. Found: C, 55.61; H, 6.31; P, 5.65. ¹H NMR (100 MHz, CD₂Cl₂): 7.51 (dd{J₁₃=8.6, J_{P-H₁}=2.0 Hz}, H₁ (upfield half obscured by Me singlet)); 8.01 (dd{J₂₃=12.2, J_{P-H₂}=1.6 Hz}, H₂); 5.14 (q{J_{P-H} < 0.5 Hz}, H₃); 7.53 and 8.77 τ (s,CH₃). ¹¹B NMR (CD₂Cl₂): 107.6(1), 17.9(1), 11.9(1), -0.12(1), -2.21(2), -9.56 ppm(1). [Ru(AP)(C₂B₇H₇Me₂)](IId), AP (0.091 g, 0.301 mmol), [Ru(PPh₃)₂(C₂B₇H₇Me₂)] (0.153 g, 0.201 mmol), 70% yield. Anal. Calcd for C₂₅H₃₂B₇PRu: C, 55.58; H, 5.97; P, 5.73. Found: C, 55.92; H, 6.07; P, 5.38. ¹H NMR (100 MHz, CD₂Cl₂): 7.52 (dd{J₁₂=3.5, J₁₃=7.5, J_{P-H₁} < 0.5 Hz}, H₁); 8.01 (dd{J₂₃=8.2, J_{P-H₂} < 0.5 Hz}, H₂); 5.58(m,H₃); 6.14(m,CH₂); 7.69 and 8.77 τ (s,CH₃). ¹³C{¹H} (20% CD₂Cl₂/CH₂Cl₂): 55.73(s,C₁), 88.76 (d{⁴J_{P-C₂}=4.1 Hz}, C₂),

39.49 ppm ($d\{^3J_{P-C} = 15.2$ Hz}, CH_2). ^{11}B NMR (CD_2Cl_2): 108.0(1), 19.2(1), 14.6(1), -2.06(3), -11.0 ppm(1). $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_8\text{Ph})](\text{IIe})$, SP (0.149 g, 0.517 mmol), $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_8\text{Ph})]$ (0.279 g, 0.344 mmol), 58% yield. Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{B}_7\text{PRu}$: C, 58.56; H, 5.26; P, 5.39. Found: C, 58.58; H, 5.42; P, 5.70. ^1H NMR (100 MHz, CD_2Cl_2): 8.55 ($dt\{J_{12} \approx 1$, $J_{13} = 8.8$, $J_{P-\text{H}_1} \approx 1$ Hz}, H_1), 7.70 ($dt\{J_{23} = 12.0$, $J_{P-\text{H}_2} \approx 1$ Hz}, H_2), 4.83 ($q\{J_{P-\text{H}_3} < 0.5$ Hz}, H_3), 4.19 τ (br,s, carborane C-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$): 65.44 ($s\{J_{\text{C}_1-\text{H}} = 155$, 162 Hz}, C_1), 92.35 ($s\{J_{\text{C}_2-\text{H}_3} = 159$ Hz}, C_2), 104.2 ppm (br,s, carborane C). ^{11}B NMR (CD_2Cl_2): 106.8(1), 15.2(1), 9.09(1), -4.82(3), -10.4 ppm(1). $[\text{Ru}(\text{MBP}(\text{C}_2\text{B}_7\text{H}_7\text{Me}_2))](\text{IIf})$, MBP (0.21 g, 0.87 mmol), $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_7\text{Me}_2)]$ (0.301 g, 0.395 mmol), 77.5% yield, m.p.: 250-280°C (dec). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{B}_7\text{PRu}$: C, 50.24; H, 6.32; P, 6.48. Found: C, 50.33; H, 6.55; P, 6.55. ^1H NMR (100 MHz, CD_2Cl_2): 7.87 ($d\{J_{13} = 8.5$ Hz}, H_1); ca. 7.3 (peak partially obscured by CH_2 resonances, H_2); 5.59(m, H_3); 6.8-7.5(m, CH_2); 7.61 and 8.42 τ (s, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$): 55.42 ($s\text{, C}_1$), 94.98 ($d\{^3J_{P-\text{C}_2} = 2.6$ Hz}, C_2), 30.1-33.4 ppm (CH_2). ^{11}B NMR (CD_2Cl_2): 107.5(1), 17.5(1), 10.6(1), 0.19(1), -2.30(1), -3.59(1), -9.65 ppm(1). $[\text{Ru}(\text{DBP}(\text{C}_2\text{B}_7\text{H}_7\text{Me}_2))](\text{IIg})$, DBP (0.19 g, 0.87 mmol), $[\text{Ru}(\text{PPh}_3)_2(\text{C}_2\text{B}_7\text{H}_7\text{Me}_2)]$ (0.302 g, 0.396 mmol), 56% yield, m.p.: 119-130°C (dec). Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{B}_7\text{PRu}$: C, 47.39; H, 7.07; P, 6.79. Found: C, 47.46; H, 7.08; P, 6.79. ^1H NMR (100 MHz, CD_2Cl_2): ca. 8.0 and 7.2 (H_1 and H_2 respectively, peaks partially obscured by CH_2 resonances); 5.07(m, H_3); 6.8-8.2(m, CH_2); 7.66 and 8.30(s, CH_3); 4.16 (m, uncoordinated H_3); 4.88 τ (m, uncoordinated H_1 and H_2). ^{13}C NMR (20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$): 54.53 ($s\{J_{\text{C}_1-\text{H}} = 142.5$, 165 Hz}, C_1), 94.65 ($s\{J_{\text{C}_2-\text{H}_3} = 156.5$ Hz}, C_2), 23.2-32.8 (alkyl), 116.28 ($d\{^4J_{P-\text{C}_1} = 22.2$ Hz}, uncoordinated C_1), 137.5 ppm ($d\{^3J_{P-\text{C}_2} = 14$ Hz}, uncoordinated C_2). ^{11}B NMR (CD_2Cl_2): 106.8(1), 17.2(1), 9.73(1), -0.11(1), -2.30(1), -4.48(1), -9.85 ppm(1). Infrared spectrum (KBr): free $\nu_{\text{C}=\text{C}}$ at 1629 cm^{-1} .

Reaction of [6-(AP)-6,2,3-RuC₂B₇H₉] with Carbon Monoxide

A toluene (1 ml) solution of $[\text{Ru}(\text{AP})(\text{C}_2\text{B}_7\text{H}_9)]$ (54.0 mg, 0.105 mmol) was

stirred under a carbon monoxide atmosphere, and the initial blood-red color turned yellow instantly. After 5 minutes petroleum ether (20 ml) was layered on top of the toluene, and the mixture was allowed to stand for 4 h undisturbed. The resulting yellow crystals were filtered in air, washed with petroleum ether, methanol and recrystallized from dichloromethane/petroleum ether affording [closo-6,6-(CO)₂-6-AP-6,2,3-RuC₂B₇H₉](IIg)](27%), m.p.: 172-176° C. Anal. Calcd for C₂₅H₂₈B₇P₂Ru: C, 52.84; H, 4.97; P, 5.45. Found: C, 53.06; H, 5.21; P, 4.97. ¹H NMR (100 MHz, CD₂Cl₂): 5.09(m, H₁), 4.96(m, H₂), 4.40(m, H₃), and 6.62 τ(m, CH₂). ¹¹B{¹H} NMR (CD₂Cl₂): 1.40(2), -9.33(1), -20.4 and -23.2 ppm (4, overlapped peaks). Infrared spectrum (KBr): ν_{CO} at 2037(s) and 1980 cm⁻¹(s) and free ν_{C=C} at 1630 cm⁻¹.

Preparation of [closo-6,6-(MBP)₂-6,2,3-RuC₂B₇H₉](IVa)

To a stirred suspension of [Ru(PPh₃)₂(C₂B₇H₉)] (0.102 mg, 0.138 mmol) in toluene (2 ml) was added (but-3-enyl)diphenylphosphine (0.078 g, 0.32 mmol). The blue solution instantly turned red. After 15 min, pentane (60 ml) was layered above the toluene solution. After standing undisturbed overnight the mixture was cooled to -15° C for 2 d, precipitating yellow crystals of [closo-6,6-(MBP)₂-6,2,3-RuC₂B₇H₉](IVa) (0.066 g, 69%) which were filtered quickly in air, washed with methanol and petroleum ether and vacuum dried, m.p.: 115-126° C (dec, darkens at 100° C). Anal. Calcd for C₃₄H₄₃B₇P₂Ru: C, 59.15; H, 6.28; P, 8.97. Found: C, 60.45; H, 6.56; P, 8.53.

¹H FTNMR (200.133 MHz, CD₂Cl₂, 33° C): 2.60(m, phenyl protons), 4.7, 6.3, 6.7(br, alkenyl protons) and 7.58 τ(br, methylene protons). At -38° C: 2.70(br,m, phenyl protons), 4.90(br, alkenyl protons) and 7.65 τ(br, methylene protons). At -68° C: 2.27, 2.56, 2.73, 2.90(m, phenyl protons), 3.54, 4.88(br,s, carborane C-H protons), 4.34(br, m, uncoordinated H₃), 5.09(br,s) and 5.16(d, J₂₋₃=10 Hz)(uncoordinated H₁ and H₂, respectively), 5.39, 5.78, 6.11(br, coordinated alkenyl protons), 7.23

and 8.17 τ (br, m, methylene protons). $^{13}\text{C}\{\text{H}\}$ FTNMR (50.32 MHz, 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$, 22°C): 133.7 (d, $^2J_{\text{P}-\text{C}}=13$ Hz, ortho phenyl carbon), 131.3 (s, para carbon), 129.8 (d, $^3J_{\text{P}-\text{C}}=10$ Hz, meta carbon) and 31.6 ppm (overlapping doublets, $J_{\text{P}-\text{C}_4}=18$ Hz, $^2J_{\text{P}-\text{C}_3}=11$ Hz, methylene carbons). At -23°C : 138 (br, uncoordinated C_2), 134-129 (complex multiplet, phenyl carbons), 115 (br, uncoordinated C_1) and 28 ppm (br, methylene carbons). At -78°C : 138.4 (d, $^3J_{\text{P}-\text{C}_2}=12$ Hz, uncoordinated C_2), 133.4-127.8 (complex multiplet, phenyl carbons), 115.3 (s, coordinated C_1), 79.3 (s, coordinated C_2), 72.7 (br, carborane carbon), 58.5 (s, coordinated C_1), 41.2 (br, carborane carbon), 35.4 (d, $J_{\text{P}-\text{C}_4}=25$ Hz) and 29.8(s)(methylene carbons of coordinated butenyl side-chain), 27.5 (d, $J_{\text{P}-\text{C}_4}=20$ Hz) and 23.2 ppm(s)(methylene carbons of uncoordinated butenyl side-chain). $^{31}\text{P}\{\text{H}\}$ FTNMR (81.02 MHz, 20% $\text{C}_6\text{D}_6-\text{C}_6\text{H}_5\text{CH}_3$, 60°C): 59.8(s) and -13.7 ppm(s). At 32°C in 20% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$: 60.3 and -14.0 ppm (br,s, $W_{1/2} \approx 200$ Hz). At -23°C : 66.8 (br,s, $W_{1/2} \approx 200$ Hz) and 42.3 ppm (br,s, $W_{1/2} \approx 650$ Hz). At -73°C : 68.5 (d, $^2J_{\text{P}-\text{P}}=32$ Hz) and 47.2 ppm(d). $^{11}\text{B}\{\text{H}\}$ FTNMR (111.8 MHz, $\text{CD}_2\text{Cl}_2, 44^\circ\text{C}$): 107.5(1), 17.3(1), 2.5(1), -5.0(2), -6.5(1) and -8.7 ppm(1). At -40°C : 20.4(2), -6.0(2) and -23.2 ppm(3). Infrared spectrum (Nujol): 3045(w), 3525(s,br), 1941(w), 1630(m), 1578(w), 1563(w), 1424(s), 1300(w), 1250(w), 1174(w), 1149(w), 1093(m,sh), 1077(m), 1053(m,sh), 1019(w), 980(m,br), 933(w), 897(m), 886(w), 786(w), 738(s), 692 cm^{-1} (s). In CH_2Cl_2 solution: Two additional weak bands at 1325 and 1285 cm^{-1} .

The complex [*cis*-6,6-(DBP)₂-6,2,3-RuC₂B₇H₉](IVb) was synthesized from DBP (0.080 g, 0.367 mmol) and [Ru(PPh₃)₂C₂B₇H₉] (0.100 g, 0.136 mmol) in 2 ml of toluene and worked up as described above. Yield: 0.062 g (70%), m.p.: 91-96°C (dec). Anal. Calcd for C_{33.5}H₅₁B₇P₂Ru (IVb-0.5 C₆H₅CH₃): C, 58.10; H, 7.47; P, 8.95. Found: C, 57.02; H, 7.39; P, 8.89. ^1H FTNMR (200.133 MHz, CD_2Cl_2 , 22°C): 2.66, 2.82 (m, phenyl protons), 4.82, 5.65, 6.42 (br, alkenyl protons) 7.92 and 8.17 τ (br, methylene protons). At 7°C : 2.61, 2.85 (m, phenyl protons), 4.42, 5.17, 5.98, 6.55 (br, overlapping alkenyl proton resonances), 7.93 and

8.15 τ(br, methylene protons). At -88°C : 2.57, 2.71 (m, phenyl protons), 3.07 (br, carborane C-H), 4.41 (br, uncoordinated H₃), 4.68 (br, uncoordinated H'₃), 4.90 (br, carborane C-H), 5.25 (complex multiplet, uncoordinated H₁, H₂, H'₁, H'₂), 6.00, 6.39, 6.68 (br, coordinated H'₁, H'₂, H'₃), 7.99, 8.15 and 8.77 ppm (br, methylene protons). $^{31}\text{C}\{^1\text{H}\}$ FTNMR (50.32 MHz, 20% CD₂Cl₂/CH₂Cl₂, 27° C): 132.9 (d, $^2J_{\text{P}-\text{C}}=8$ Hz, ortho phenyl carbon), 131.0 (s, para carbon) 129.6 (d, $^3J_{\text{P}-\text{C}}=8$ Hz, meta carbon) and 28.5 ppm (overlapping doublet and singlet, $J_{\text{P}-\text{C}_4}=15$ Hz, methylene carbons). At -23°C : 138.7 (d, $^4J_{\text{P}-\text{C}_2}=12$ Hz, uncoordinated C₂), 132.4, 130.7, 129.3 (s, phenyl carbons), 115.5 (s, uncoordinated C₁), 28.9 (overlapping doublet and singlet, $J_{\text{P}-\text{C}}=19$ Hz) and 26.6 ppm (d, $J_{\text{P}-\text{C}}=20$ Hz) (methylene carbons). At -83°C : 141.8 (s, uncoordinated C'₂), 138.3 (s, uncoordinated C'₂), 133.6, 132.2, 131.0, 130.3, 129.5, 128.6 (br,s, phenyl carbons), 118.8 (s, uncoordinated C'₁), 115.2 (s, uncoordinated C'₁), 75.9 and 39.2 (br,s, carborane carbons), 73.3 and 51.5 (s, coordinated C'₂ and C'₁ respectively), 32.5, 30.9, 29.1, 27.6, 25.1 and 21.3 ppm (br,s, methylene carbons). $^{31}\text{P}\{^1\text{H}\}$ FTNMR (81.02 MHz, 20% CD₂Cl₂/CH₂Cl₂, 47° C): 42.8 ppm (br,s, $W_{1/2}^1 \approx 160$ Hz). At -3°C : 46.4 ppm (br,s, $W_{1/2}^1 \approx 1200$ Hz). At -88°C : 61.0 (d, $^2J_{\text{P}-\text{P}}=37$ Hz) and 36.5 ppm(d). $^{11}\text{B}\{^1\text{H}\}$ FTNMR (111.8 MHz, CD₂Cl₂, 44° C): 2.6(3) and -15.8 ppm(4). At -71°C : 24.9(2), -3.4(2) and -19.9 ppm(3). Infrared spectrum (KBr): $\nu_{\text{C}=\text{C}}$ (uncoordinated) at 1633 cm⁻¹.

Preparation of [closo-6-CO-6,6-(DBP)₂-6,2,3-RuC₂B₇H₉](Vb)

Dry carbon monoxide was bubbled through a solution of [Ru(DBP)₂C₂B₇H₉] (IIIb) (0.150 g, 0.232 mmol) in toluene (5 ml) yielding a bright yellow solution. Upon addition of petroleum ether (10 ml) and cooling to -15° C for 1 d, yellow crystals of [closo-6-CO-6,6-(DBP)₂-6,2,3-RuC₂B₇H₉](Vb) (0.133 g, 87%) were obtained, m.p.: 121-123° C . Anal. Calcd for C₃₁H₄₇B₇P₂ORu: C, 55.21; H, 7.02; P, 9.18. Found: C, 54.78; H, 7.14; P, 9.66. ^1H FTNMR (200.133 MHz, C₆D₆):

2.40 (m,2H), 2.60 and 2.98 (m,4H)(phenyl protons), 4.52(m,4H,H₃), 5.11 (d, J₁₃=11 Hz, 4H,H₁), 5.17 (d, J₂₃=24 Hz, 4H,H₂), 6.59 (br,s,2H, carborane C-H), 8.11 and 8.60 τ(m,8H, methylene protons). ³¹P{¹H} FTNMR (81.02 MHz, 20% CD₂Cl₂-CH₂Cl₂): 29.7 ppm(s). ¹¹B{¹H} FTNMR (80.5 MHz, CD₂Cl₂): 0.00(2), -9.13(1) and -23.4 ppm(4). Infrared spectrum (KBr): ν_{CO} at 1930(s,br), and ν_{C=C} (uncoordinated) at 1632 cm⁻¹(s).

The complex [closo-6-CO-6,6-(MBP)₂-6,2,3-RuC₂B₇H₉](Va)(70 mg, 77%) was similarly prepared from [Ru(MBP)₂(C₂B₇H₉)](93 mg, 0.13 mmol) at -78°C. m.p.: 174-176°C (melts to a red liquid, darkens at 165°C). Anal. Calcd for C₃₅H₄₃B₇P₂ORu: C, 58.52; H, 6.03; P, 8.62. Found: C, 58.18; H, 6.15; P, 8.33. ¹H FTNMR (200.133 MHz, C₆D₆): 2.42 (m,4H), 2.89 and 3.08 (m,8H)(phenyl protons), 4.63 (m,2H,H₃), 5.18 (d, J₁₃=10 Hz, 2H, H₁), 5.25 (d, J₂₃=17 Hz, 2H, H₂), 6.70 (br,s,2H, carborane C-H), 7.79 and 8.04 τ(m,4H, methylene protons). ³¹P{¹H} FTNMR (81.02 MHz, 20% C₆D₆/C₆H₆): 42.5(s). ¹¹B{¹H} FTNMR (80 MHz, CD₂Cl₂): 0.4(2), -8.2(1) and -22.0 ppm(4). Infrared spectrum (KBr): ν_{CO} at 1932 (s,br) and ν_{C=C} (uncoordinated) at 1628 cm⁻¹(w). The carbonylation of IVa was monitored by ³¹P{¹H} FTNMR at several temperatures using rubber septa and a syringe needle. ([IVa] ≈ 0.03M). At -78°C in 10% C₆D₆-C₆H₅CD₃: 45.0 ppm(s). At 30°C in 10% C₆D₆-C₆H₆: 45.4 (s,1), 42.5 (s,5) and -15.3 ppm (s,1) (≈30% IIIb). At 60°C in 10% C₆D₆-C₆H₅CD₃: (The sample was carbonylated at 60°C and the spectrum recorded at 30°C) 45.5 (s,1), 42.5 (s,2) and -15.3 ppm (s,1) (≈50% IIIb). Infrared spectrum of IIIb (Nujol): ν_{CO} at 1970 and 2025 cm⁻¹.

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38. The carboranyl carbon and carboranyl C-H proton resonances for IVa-b were only observed at low temperatures, presumably due to the fluxional processes which occur at higher temperatures.
39. This value agrees well with the more approximate values obtained from the ^{13}C { ^1H } and ^1H FTNMR spectra for the same process.
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45. $R = [\sum ||Fo_i - |Fc_i|| / \sum |Fc_i|]$; $R_w = [\sum w ||Fo_i - |Fc_i||^2 / \sum w |Fc_i|^2]^{1/2}$; $w = 1(\sigma F)^2$. The function $\sum w ||Fo_i - |Fc_i||^2$ was minimized in least-squares refinement.
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- Figure 1
- A. The 100 MHz ^1H NMR spectrum of $[\text{Ru}(\text{SP})(\text{C}_2\text{B}_7\text{H}_9)](\text{IIa})$ in CD_2Cl_2 .
 - B. Same with ^{31}P -decoupling (triplet at 4.72τ is due to residual CHDCl_2)

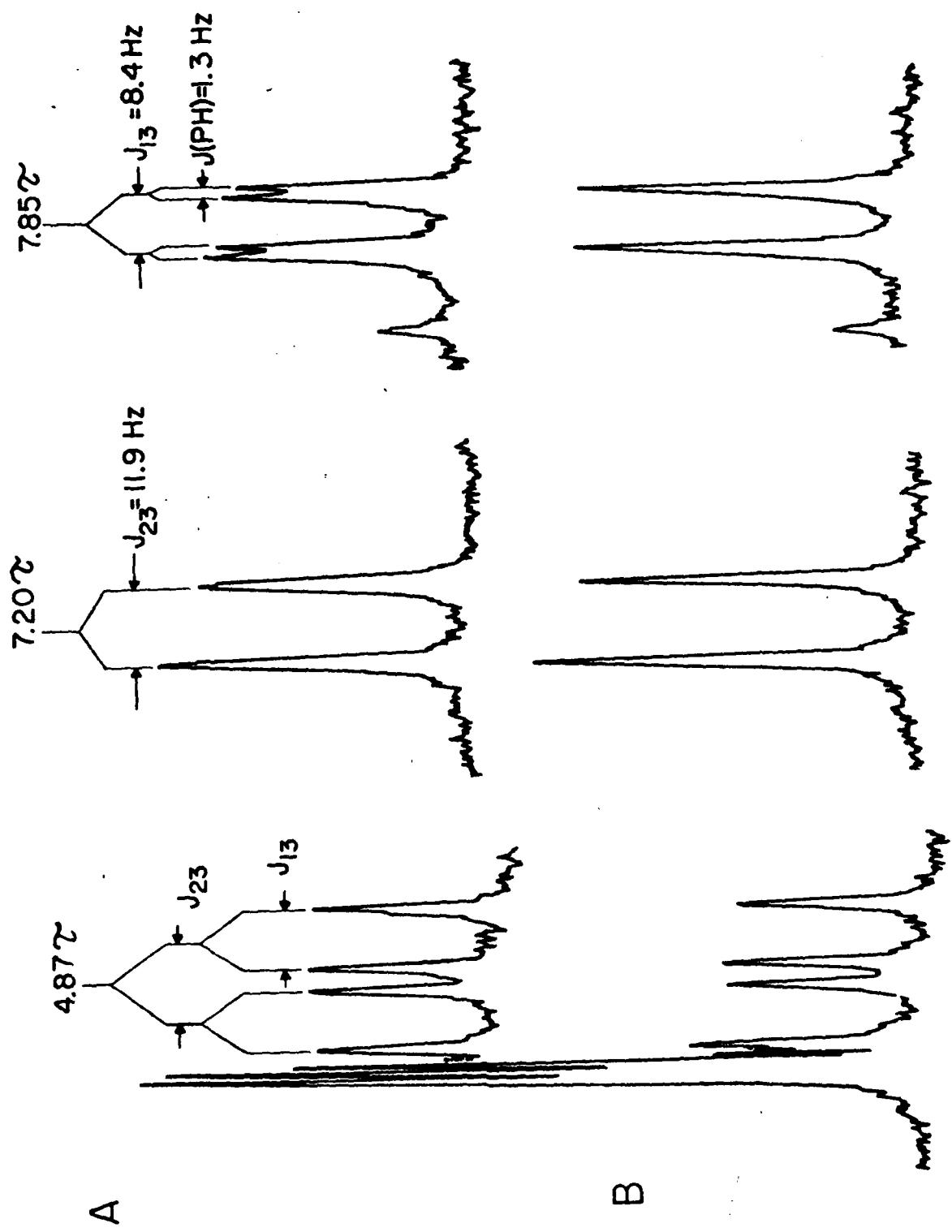


Figure 2 Structure of [hyper-closo-2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-Ru-C₂B₇H₇](IId) and the numbering system employed. Atoms are shown as 50% probability ellipsoids. For the two phenyl rings, only the positions are indicated, and all hydrogen atoms have been removed for clarity.

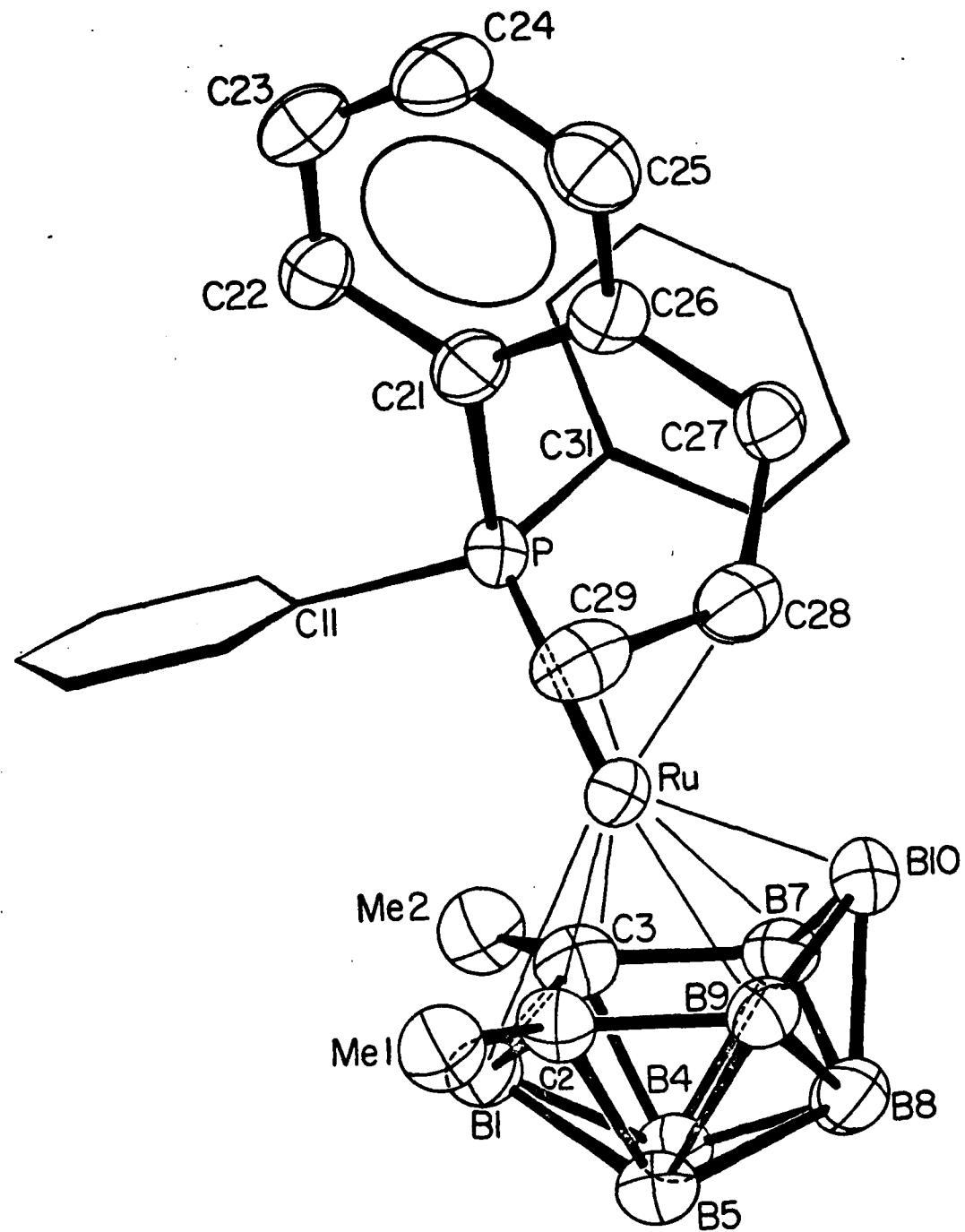


Figure 3 $^{31}\text{P}\{^1\text{H}\}$ FTNMR spectra of [closo-Ru(MBP)₂C₂B₇H₉], IVa, in 20% CD₂Cl₂/CH₂Cl₂. The spectrum marked by asterisk was recorded in 10% C₆D₆-C₆H₅CH₃. Scale is in ppm downfield from D₃PO₄.

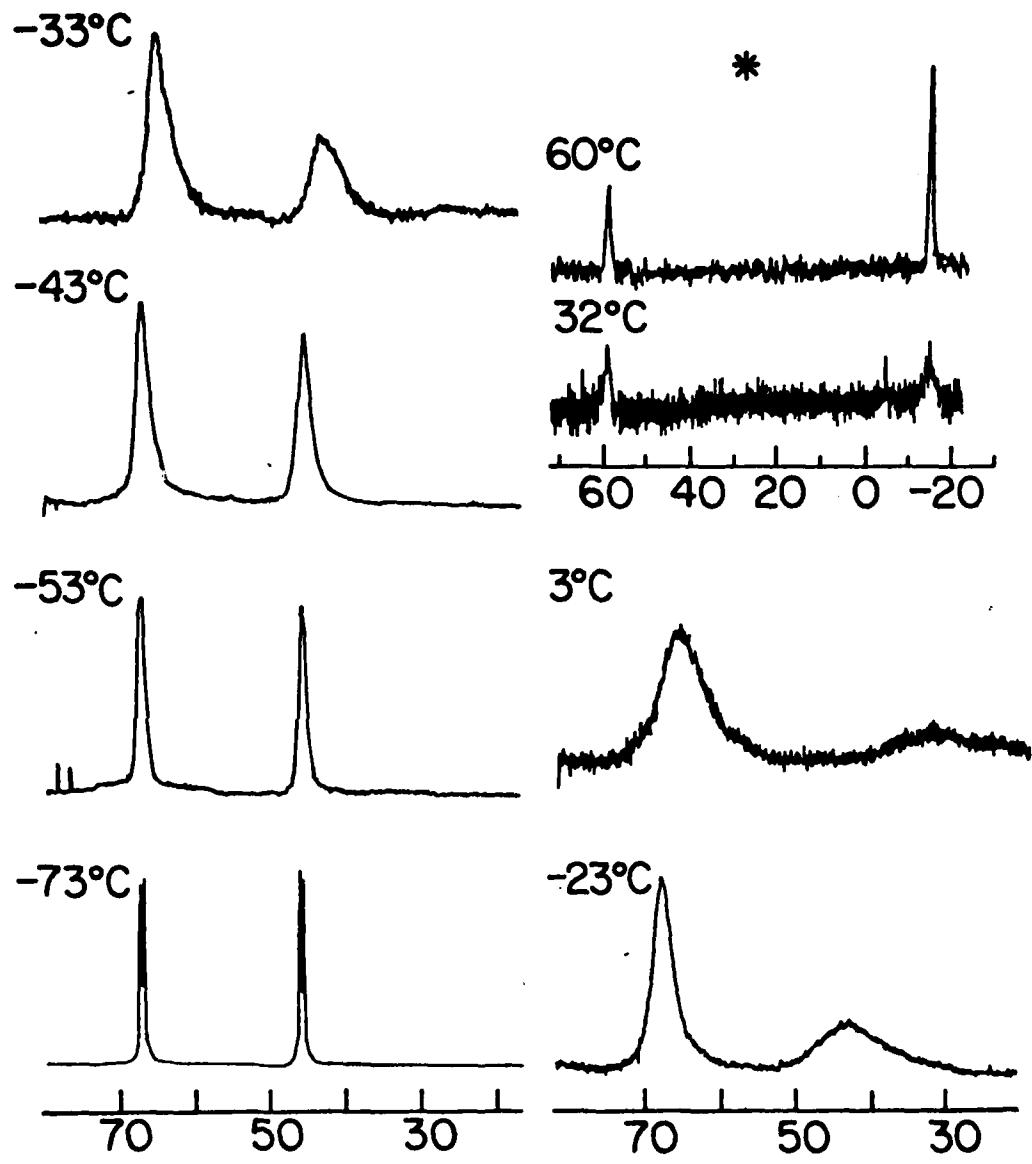


Figure 4 $^{31}\text{P}\{\text{H}\}$ FTNMR spectra of [closo-Ru(DBP)₂C₂B₇H₉], IVb, in 20% CD₂Cl₂/CH₂Cl₂. Scale is in ppm downfield from D₃PO₄.

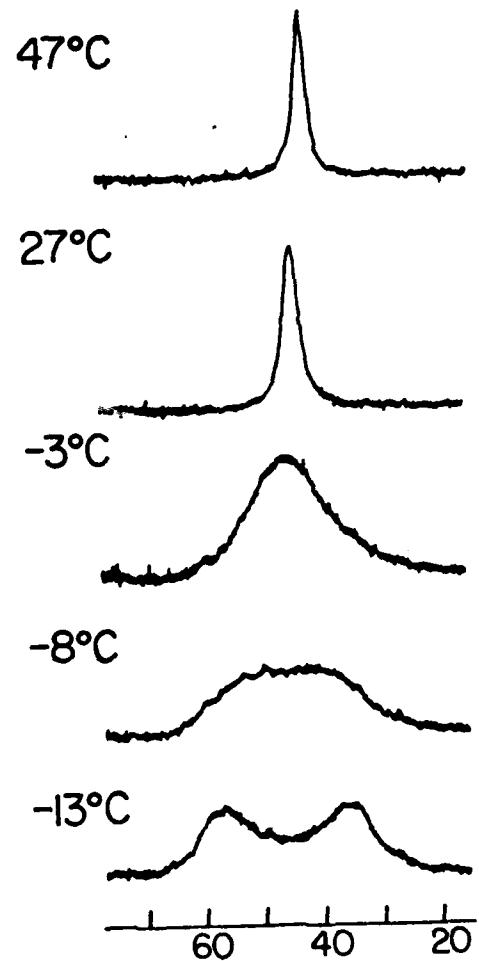
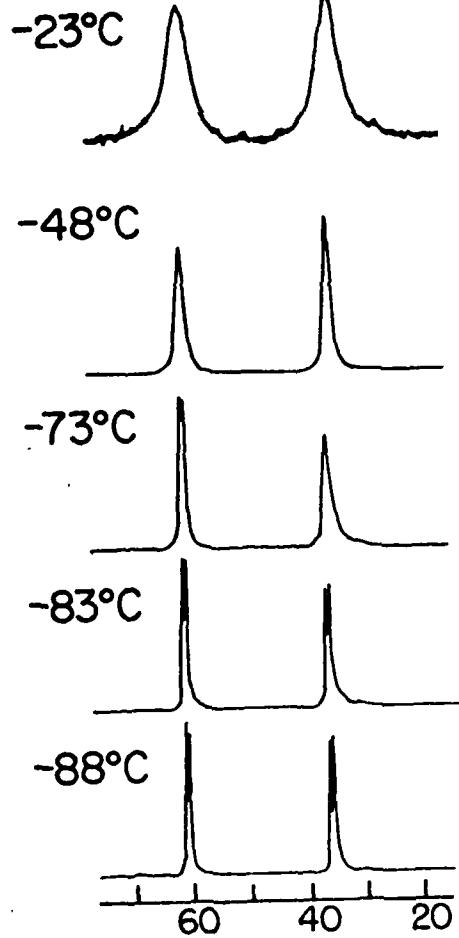
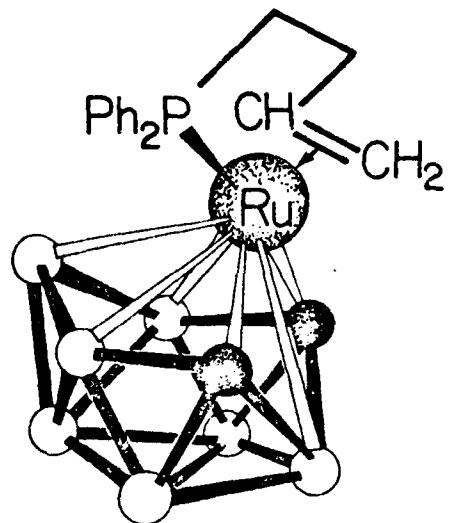
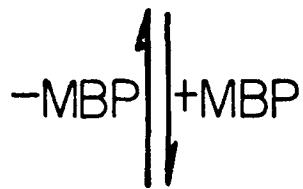


Figure 5 Proposed dynamic processes for [c_{los}-Ru(MBP)₂C₂B₇H₉], IVa.



30°C red solution
hyper-closo

● CH
○ BH



-50°C yellow
solution — creso

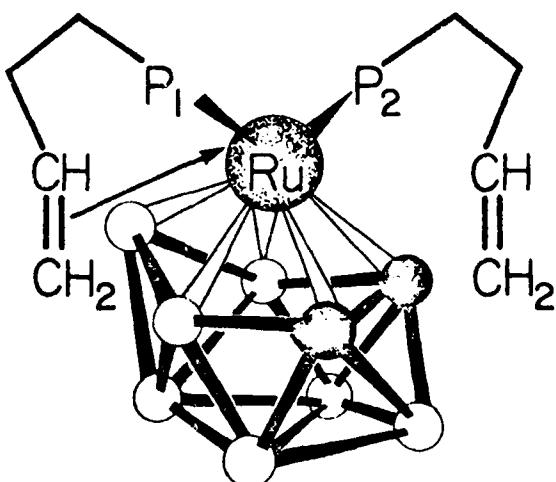
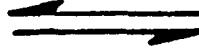
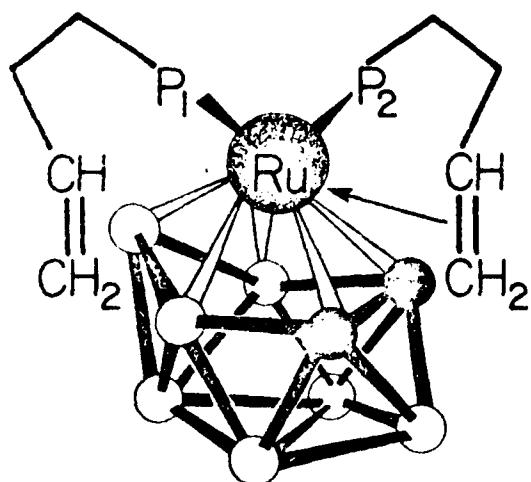


Figure 6 $^{13}\text{C}\{^1\text{H}\}$ FTNMR spectra of [closo-Ru(DBP)₂C₂B₇H₉], IVb, in 20% CD₂Cl₂-CH₂Cl₂ (extra solvent peak at -83°C is due to small amounts of solid CD₂Cl₂/CH₂Cl₂).

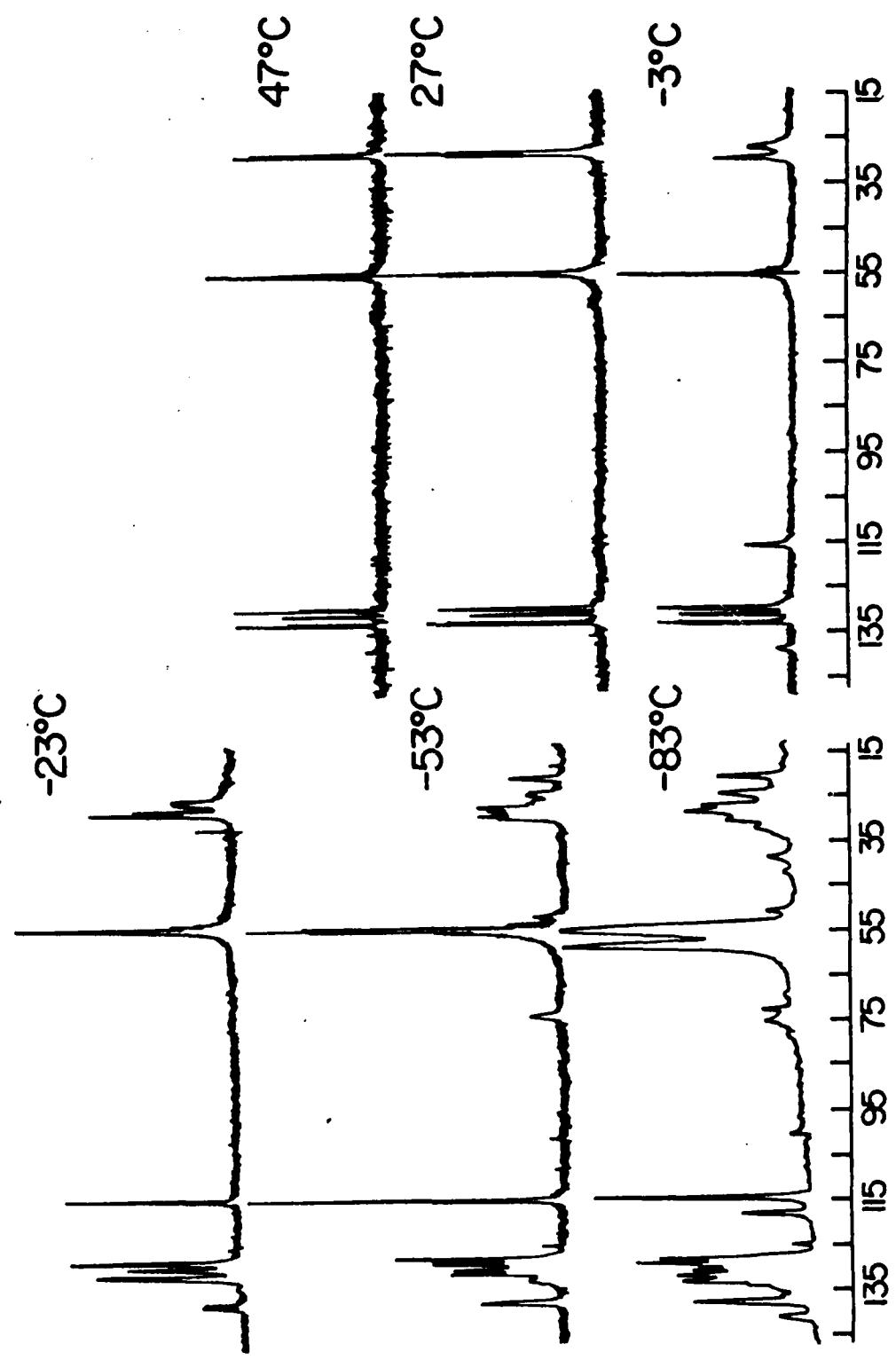


Figure 7 ^1H FTNMR spectra of IVb in CD_2Cl_2 . Resonances marked by asterisks are due to residual CH_2Cl_2 and toluene of crystallization.

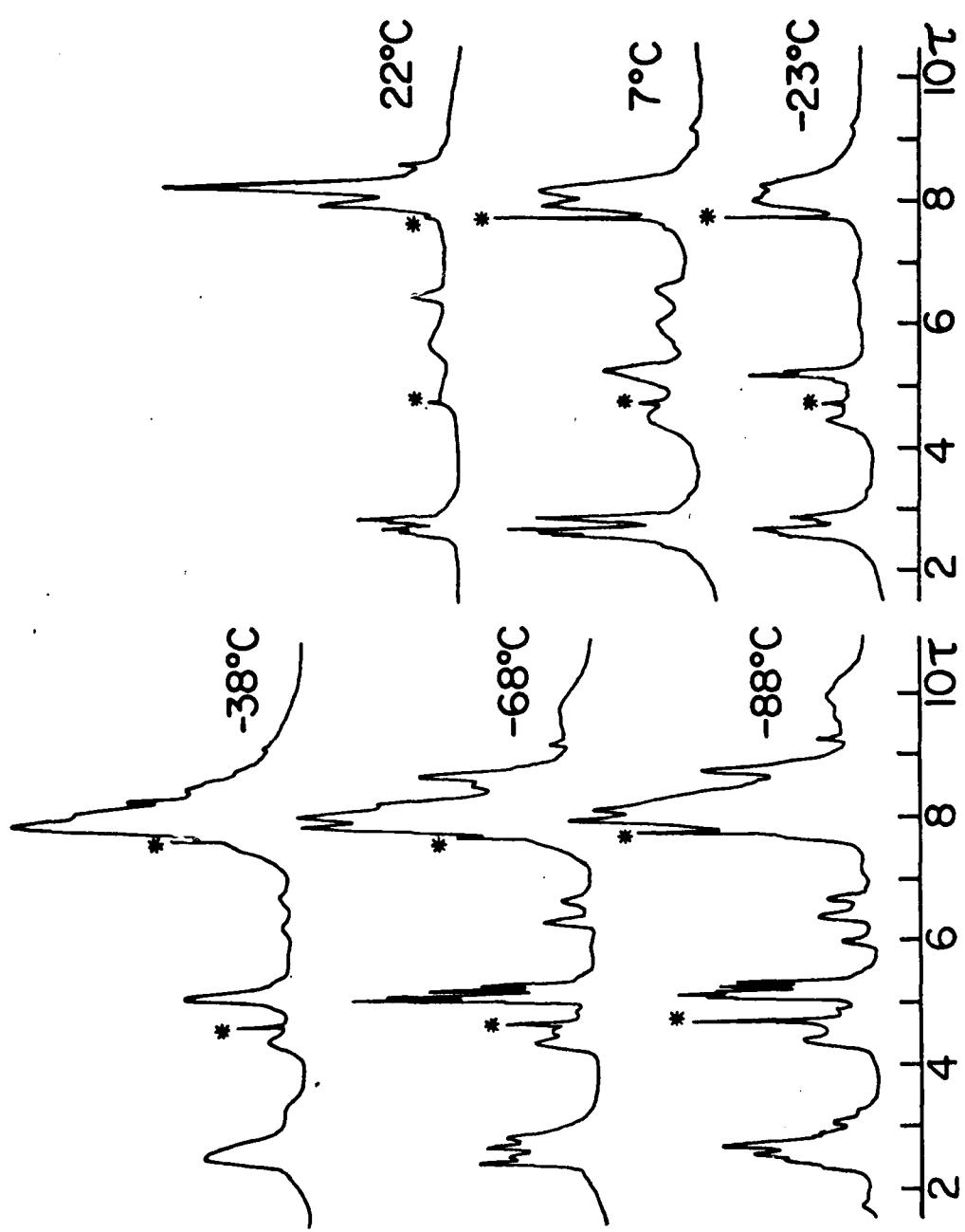
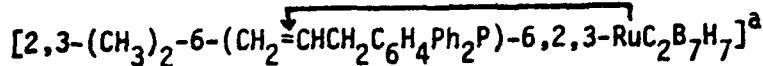


TABLE I

Atomic Positional Parameters in



<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Ru	-0.08832(4) ^b	0.23399(2)	0.17700(2)
P	-0.15648(11)	0.23507(7)	0.04155(6)
B(1)	-0.1975(6)	0.3612(3)	0.1937(3)
B(4)	-0.3551(6)	0.2987(4)	0.1727(3)
B(5)	-0.1548(6)	0.3089(3)	0.2843(3)
B(7)	-0.3555(6)	0.2025(4)	0.1242(4)
B(8)	-0.2486(7)	0.2009(4)	0.2395(4)
B(9)	-0.0303(6)	0.2185(3)	0.3050(3)
B(10)	-0.1602(6)	0.1430(3)	0.2111(3)
C(2)	-0.0176(5)	0.3131(3)	0.2798(3)
C(3)	-0.3263(5)	0.2968(3)	0.1072(3)
C(21)	0.0166(5)	0.1999(3)	0.0609(3)
C(22)	0.0605(5)	0.2452(3)	0.0248(3)
C(23)	0.1907(6)	0.2151(3)	0.0393(3)
C(24)	0.2768(6)	0.1394(4)	0.0894(4)
C(25)	0.2346(6)	0.0944(3)	0.1256(4)
C(26)	0.1052(5)	0.1233(3)	0.1126(3)
C(27)	0.0672(6)	0.0757(3)	0.1562(4)
C(28)	0.0936(5)	0.1316(3)	0.2244(3)
C(29)	0.1741(5)	0.2140(3)	0.2580(3)
H(1) ^c	-0.199(7)	0.431(4)	0.184(4)
H(4)	-0.466(7)	0.322(4)	0.150(4)
H(5)	-0.119(7)	0.345(4)	0.341(4)

Table I (cont'd)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
H(7)	-0.470(7)	0.164(4)	0.068(4)
H(8)	-0.295(7)	0.162(4)	0.259(4)
H(9)	0.078(7)	0.184(4)	0.368(4)
H(10)	-0.134(7)	0.074(4)	0.225(4)
H(22)	0.001(8)	0.299(4)	-0.007(4)
H(23)	0.221(8)	0.242(4)	0.015(4)
H(24)	0.360(7)	0.118(4)	0.100(4)
H(25)	0.292(8)	0.044(4)	0.162(4)
H(271)	0.143(7)	0.022(4)	0.188(4)
H(272)	-0.052(8)	0.055(4)	0.109(4)
H(28)	0.121(7)	0.097(4)	0.274(4)
H(291)	0.196(8)	0.242(4)	0.230(4)
H(292)	0.231(8)	0.225(4)	0.316(4)

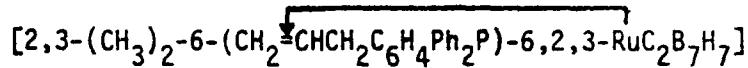
^aAtomic positional parameters for atoms which have been treated as members of rigid groups are listed in Table II.

^bThe numbers given in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits.

^cHydrogen atoms are numbered according to the number of the atom to which they are bonded.

TABLE II

a) Atomic Positional Parameters for Members of Rigid Groups in



<u>Group</u>	<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Phenyl 1	C(11)	-0.1902	0.3495	0.0058
	C(12)	-0.3348	0.3804	-0.0805
	C(13)	-0.3540	0.4699	-0.0995
	C(14)	-0.2285	0.5286	-0.0321
	C(15)	-0.0839	0.4977	0.0543
	C(16)	-0.0647	0.4082	0.0732
	H(12)	-0.425	0.338	-0.129
	H(13)	-0.458	0.492	-0.162
	H(14)	-0.242	0.593	-0.046
	H(15)	0.006	0.540	0.103
	H(16)	0.039	0.386	0.135
Phenyl 3	C(31)	-0.3302	0.1692	-0.0579
	C(32)	-0.3778	0.1763	-0.1381
	C(33)	-0.5033	0.1220	-0.2114
	C(34)	-0.5813	0.0606	-0.2044
	C(35)	-0.5337	0.0536	-0.1242
	C(36)	-0.4081	0.1079	-0.0509
	H(32)	-0.322	0.220	-0.143
	H(33)	-0.538	0.127	-0.269
	H(34)	-0.672	0.022	-0.257
	H(35)	-0.590	0.009	-0.119
	H(36)	-0.374	0.103	0.007
Methyl 1	C(41)	0.1430	0.3679	0.3493
	H(411)	0.149	0.410	0.317
	H(412)	0.143	0.401	0.389
	H(413)	0.243	0.328	0.388

Table II (cont'd)

<u>Group</u>	<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
Methyl 2	C(51)	-0.4622	0.3372	0.0130
	H(511)	-0.564	0.336	0.000
	H(512)	-0.438	0.399	0.010
	H(513)	-0.484	0.300	-0.033

b) Group Parameters for Rigid Groups^a

<u>Group</u>	<u>x</u> (Å)	<u>y</u> (Å)	<u>z</u> (Å)	<u>ϕ</u> (deg)	<u>θ</u> (deg)	<u>ρ</u> (deg)
Phenyl 1	-0.1902(3)	0.3495(1)	0.0058(2)	-59.2(3)	-110.1(1)	-144.2(3)
Phenyl 3	-0.3302(3)	0.1692(2)	-0.0579(2)	120.6(1)	-147.8(1)	-113.6(1)
Methyl 1	0.1429(6)	0.3679(3)	0.3493(3)	138(3)	-132(3)	91(4)
Methyl 2	-0.4622(6)	0.3372(3)	0.0130(3)	-81(2)	172(3)	-114(3)

^aThese parameters are defined in reference 34.

TABLE III

Atomic Thermal Parameters in $[2,3-(\text{CH}_3)_2-6-(\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{Ph}_2\text{P})-6,2,3-\text{RuC}_2\text{B}_7\text{H}_7]^3$

<u>Atom</u>	<u>β_{11}</u>	<u>β_{22}</u>	<u>β_{33}</u>	<u>β_{12}</u>	<u>β_{13}</u>	<u>β_{23}</u>
Ru	802(5)	255(1)	239(1)	7(2)	310(2)	20(1)
P	866(14)	226(4)	265(4)	-16(7)	349(7)	7(4)
B(1)	1223(80)	301(24)	327(23)	29(33)	467(38)	9(18)
B(4)	1219(81)	429(25)	374(24)	1(36)	527(40)	-29(20)
B(5)	1339(83)	350(25)	344(23)	-8(36)	519(40)	-17(19)
B(7)	1075(77)	423(25)	405(26)	-125(36)	499(41)	-86(21)
B(8)	1497(90)	376(24)	408(26)	-148(38)	623(44)	-56(20)
B(9)	1320(79)	326(26)	305(22)	10(34)	483(37)	24(18)
B(10)	1409(86)	272(23)	411(25)	-105(34)	589(43)	-28(19)
C(2)	1141(66)	293(20)	276(18)	-49(28)	397(31)	-19(14)
C(3)	913(62)	409(21)	289(19)	54(28)	367(31)	10(16)
C(21)	923(60)	271(17)	316(19)	-17(25)	403(30)	-13(14)
C(22)	1176(66)	348(23)	312(19)	-20(28)	445(32)	14(15)
C(23)	1348(74)	496(28)	449(24)	-69(34)	653(39)	6(19)
C(24)	1394(85)	616(31)	555(29)	155(40)	725(46)	54(23)
C(25)	1704(92)	413(26)	576(29)	303(38)	778(47)	136(21)
C(26)	1299(72)	303(20)	415(22)	74(29)	576(36)	27(16)
C(27)	1858(90)	291(21)	591(28)	248(35)	879(47)	149(19)
C(28)	1396(78)	377(23)	426(24)	321(33)	610(39)	161(18)
C(29)	969(67)	539(30)	327(21)	193(33)	381(34)	90(19)

<u>Group</u>	<u>Atom</u>	<u>$B (\text{\AA}^2)$</u>	<u>Group</u>	<u>Atom</u>	<u>$B (\text{\AA}^2)$</u>
Phenyl 1	C(11)	2.58(7)	Phenyl 3	C(31)	2.61(7)
	C(12)	3.48(8)		C(32)	3.48(8)
	C(13)	4.66(11)		C(33)	4.44(10)
	C(14)	5.11(11)		C(34)	4.38(10)
	C(15)	4.75(11)		C(35)	4.26(10)
	C(16)	3.50(8)		C(36)	3.37(8)
			Methyl 1	C(41)	3.74(9)
			Methyl 2	C(51)	3.97(9)

Table III (cont'd)

^aAll values of β have been multiplied by 10^5 . The anisotropic temperature factor expression is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The hydrogen atoms were assigned fixed isotropic thermal parameters: all cage hydrogen atoms had B values fixed at 5.0 \AA^2 , all other hydrogen atoms which are not members of rigid groups also were assigned $B=5.0 \text{ \AA}^2$, all methyl group hydrogen atoms were assigned B values 1.0 \AA^2 greater than the B value on the adjacent carbon atom, and all phenyl group hydrogen atoms were assigned B values 0.5 \AA^2 greater than those of the adjacent carbon atoms.

Supplementary Material

TABLE IV

Root-Mean-Square Amplitudes of Vibration and Equivalent B Values^a

Atom	R.M.S. Amplitude (Å)			Equivalent B (Å ²)		
	<u>Min.</u>	<u>Median</u>	<u>Max.</u>	<u>Min.</u>	<u>Median</u>	<u>Max.</u>
Ru	0.1581(5)	0.1636(5)	0.1791(5)	1.97	2.11	2.53
P	0.158(2)	0.168(1)	0.176(1)	1.97	2.22	2.45
B(1)	0.186(7)	0.187(7)	0.201(6)	2.72	2.77	3.19
B(4)	0.178(7)	0.202(7)	0.227(7)	2.52	3.22	4.08
B(5)	0.183(7)	0.204(7)	0.207(6)	2.64	3.28	3.39
B(7)	0.173(7)	0.198(7)	0.239(7)	2.37	3.10	4.52
B(8)	0.184(7)	0.195(7)	0.235(7)	2.70	3.00	4.36
B(9)	0.170(7)	0.198(8)	0.208(6)	2.27	3.10	3.42
B(10)	0.168(7)	0.201(7)	0.219(6)	2.24	3.18	3.78
C(2)	0.171(6)	0.184(6)	0.203(6)	2.31	2.68	3.25
C(3)	0.169(6)	0.184(6)	0.220(6)	2.25	2.66	3.84
C(21)	0.167(6)	0.177(6)	0.190(6)	2.20	2.47	2.85
C(22)	0.180(6)	0.193(6)	0.207(6)	2.56	2.94	3.40
C(23)	0.161(6)	0.223(6)	0.244(7)	2.04	3.93	4.70
C(24)	0.172(6)	0.243(6)	0.274(7)	2.34	4.68	5.95
C(25)	0.179(7)	0.226(6)	0.272(6)	2.52	4.05	5.83
C(26)	0.178(6)	0.194(6)	0.216(6)	2.50	2.97	3.68
C(27)	0.163(7)	0.194(6)	0.272(6)	2.09	2.96	5.83
C(28)	0.157(6)	0.192(6)	0.257(6)	1.95	2.91	5.21
C(29)	0.164(6)	0.206(6)	0.259(7)	2.13	3.35	5.29

^aThe equivalent B values are related to the root-mean-square amplitudes of vibration, $(\bar{U}^2)^{1/2}$, by the expression $B = 8\pi^2(\bar{U}^2)$.

Supplementary Material

TABLE V

Structure Factor Amplitudes for [2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇]

C. W. Jung, R. T. Baker, C. B. Knobler, and M. F. Hawthorne

The table lists the values of h, k, l, 10 F_o and F_c for each observed reflection.

B	L	PO	PC	B	L	PO	PC	B	L	PO	PC	B	L	PO	PC	B	L	PO	PC
***	0	213	300	-7	-7	500	510	-1	20	184	168	-1	2	20	22	-1	12	506	483
-15	22	223	322	-7	-7	201	223	0	26	450	436	-1	12	22	24	-1	12	218	228
-15	12	158	301	-7	-7	255	269	0	8	824	819	-1	12	22	24	-1	12	217	223
-14	16	226	302	-7	-7	586	608	1	12	927	936	-1	11	22	24	-1	12	310	320
-14	20	224	301	-7	-7	1273	1286	0	14	556	494	-1	11	22	24	-1	12	344	342
-14	24	228	174	-7	-7	508	514	1	16	174	189	-1	11	22	24	-1	12	310	291
-13	12	283	153	-7	-7	751	766	1	18	492	485	-1	11	22	24	-1	12	343	382
-13	16	283	186	-7	-7	295	325	1	20	189	182	-1	11	22	24	-1	12	319	394
-13	18	293	303	-6	-6	341	326	1	22	451	465	-1	11	22	24	-1	12	406	469
-13	22	296	411	-6	-6	306	314	1	24	528	588	-1	11	22	24	-1	12	403	429
-13	26	369	107	-6	-6	967	948	1	26	451	465	-1	11	22	24	-1	12	411	411
-12	12	513	331	-6	-6	432	446	1	28	528	534	-1	11	22	24	-1	12	361	360
-12	16	561	131	-6	-6	754	766	1	30	434	425	-1	11	22	24	-1	12	573	573
-12	18	375	345	-6	-6	1261	1215	1	32	186	172	-1	11	22	24	-1	12	120	120
-12	22	401	394	-6	-6	208	215	1	34	735	697	-1	11	22	24	-1	12	401	115
-12	26	465	237	-6	-6	887	846	1	36	108	1091	-1	11	22	24	-1	12	361	360
-11	10	556	195	-6	-6	698	690	1	38	31	154	-1	10	22	24	-1	10	575	575
-11	12	100	136	-6	-6	549	559	1	40	553	563	-1	10	22	24	-1	10	120	120
-11	16	636	512	-6	-6	240	278	1	42	290	290	-1	10	22	24	-1	10	401	401
-11	18	727	351	-6	-6	563	676	1	44	107	1061	-1	10	22	24	-1	10	317	317
-11	22	283	297	-6	-6	174	680	1	46	218	222	-1	10	22	24	-1	10	519	362
-11	26	264	247	-6	-6	680	615	1	48	378	370	-1	10	22	24	-1	10	360	360
-10	12	647	669	-6	-6	121	1054	1	50	409	417	-1	10	22	24	-1	10	271	271
-10	16	727	367	-6	-6	454	465	1	52	123	112	-1	10	22	24	-1	10	401	117
-10	20	283	367	-6	-6	1232	1292	1	54	474	494	-1	10	22	24	-1	10	319	319
-10	24	226	149	-6	-6	611	667	1	56	499	494	-1	10	22	24	-1	10	269	269
-10	28	551	351	-6	-6	211	230	1	58	501	458	-1	10	22	24	-1	10	247	247
-10	32	283	297	-6	-6	736	776	1	60	450	450	-1	10	22	24	-1	10	319	319
-10	36	647	149	-6	-6	482	492	1	62	207	225	-1	10	22	24	-1	10	714	714
-10	40	727	351	-6	-6	1039	1053	1	64	296	296	-1	10	22	24	-1	10	480	480
-10	44	283	367	-6	-6	1339	1337	1	66	538	537	-1	10	22	24	-1	10	96	96
-10	48	529	544	-6	-6	519	545	1	68	406	515	-1	10	22	24	-1	10	309	309
-10	52	836	343	-6	-6	219	217	1	70	363	372	-1	10	22	24	-1	10	545	484
-10	56	103	151	-6	-6	1385	1407	1	72	299	326	-1	10	22	24	-1	10	669	596
-10	60	260	260	-6	-6	713	722	1	74	117	117	-1	10	22	24	-1	10	125	125
-10	64	181	217	-6	-6	547	541	1	76	117	117	-1	10	22	24	-1	10	530	530
-10	68	825	825	-6	-6	699	699	1	78	117	117	-1	10	22	24	-1	10	132	132
-10	72	320	309	-6	-6	1075	1058	1	80	117	117	-1	10	22	24	-1	10	206	206
-10	76	609	839	-6	-6	980	966	1	82	117	117	-1	10	22	24	-1	10	185	185
-10	80	178	119	-6	-6	1357	1405	1	84	117	117	-1	10	22	24	-1	10	399	396
-10	84	905	155	-6	-6	610	320	1	86	117	117	-1	10	22	24	-1	10	167	180
-10	88	319	225	-6	-6	420	241	1	88	117	117	-1	10	22	24	-1	10	581	581
-10	92	385	373	-6	-6	568	594	1	90	117	117	-1	10	22	24	-1	10	805	798
-10	96	212	212	-6	-6	2110	2152	1	92	117	117	-1	10	22	24	-1	10	317	329
-10	100	902	374	-6	-6	81	91	1	94	117	117	-1	10	22	24	-1	10	101	91
-10	104	159	547	-6	-6	1509	1519	1	96	117	117	-1	10	22	24	-1	10	1451	1400
-10	108	1043	1043	-6	-6	1452	1463	1	98	117	117	-1	10	22	24	-1	10	227	227
-10	112	346	337	-6	-6	593	624	1	100	117	117	-1	10	22	24	-1	10	482	476
-10	116	492	492	-6	-6	2157	2232	1	102	117	117	-1	10	22	24	-1	10	621	621
-10	120	830	106	-6	-6	1361	1346	1	104	117	117	-1	10	22	24	-1	10	138	138
-10	124	474	474	-6	-6	1949	1929	1	106	117	117	-1	10	22	24	-1	10	560	560
-10	128	210	210	-6	-6	261	261	1	108	117	117	-1	10	22	24	-1	10	116	149
-10	132	229	229	-6	-6	533	535	1	110	117	117	-1	10	22	24	-1	10	480	491
-7	0	494	501	-6	-6	472	454	1	112	117	117	-1	10	22	24	-1	10	126	154

H	L	P0	PC	H	L	P0	PC	H	L	P0	PC	H	L	P0	PC	H	L	P0	PC
-7	1	119	135	-3	-3	-3	-3	2	6	801	795	-11	6	499	502	212	222	212	212
-7	4	1011	1034	637	636	110	100	10	8	184	198	-11	8	222	212	122	113	113	113
-7	6	114	100	922	922	1164	1164	11	10	1096	1073	-11	9	113	113	122	113	113	113
-7	8	899	922	195	195	358	358	12	12	103	105	-11	12	13	13	14	14	14	14
-7	10	1152	1164	357	357	193	193	13	14	444	439	-11	12	13	13	14	14	14	14
-7	12	193	195	664	664	109	109	14	14	137	163	-11	11	12	12	13	13	14	14
-7	14	666	666	357	357	213	213	15	15	266	282	-11	11	12	12	13	13	14	14
-7	16	101	101	807	807	818	818	16	16	149	145	-11	11	12	12	13	13	14	14
-7	18	198	233	926	926	223	223	17	17	1131	1140	-11	10	11	11	12	12	13	13
-7	20	233	233	408	408	410	410	18	18	415	422	-11	10	11	11	12	12	13	13
-7	22	276	276	192	192	247	247	19	19	134	145	-11	10	11	11	12	12	13	13
-7	24	339	339	12	12	286	286	20	20	1173	1140	-11	10	11	11	12	12	13	13
-7	26	369	369	554	554	366	366	21	21	568	569	-11	10	11	11	12	12	13	13
-7	28	238	238	113	113	173	173	22	22	312	302	-11	10	11	11	12	12	13	13
-7	30	173	173	102	102	237	237	23	23	367	362	-11	10	11	11	12	12	13	13
-7	32	475	475	807	807	936	936	24	24	313	303	-11	10	11	11	12	12	13	13
-7	34	139	139	276	276	410	410	25	25	708	692	-11	10	11	11	12	12	13	13
-7	36	187	187	192	192	247	247	26	26	626	630	-11	10	11	11	12	12	13	13
-7	38	348	348	12	12	286	286	27	27	996	981	-11	10	11	11	12	12	13	13
-7	40	850	850	554	554	366	366	28	28	450	444	-11	10	11	11	12	12	13	13
-7	42	139	139	187	187	138	138	29	29	119	111	-11	10	11	11	12	12	13	13
-7	44	475	475	334	334	260	260	30	30	104	111	-11	10	11	11	12	12	13	13
-7	46	1471	1471	1482	1482	538	538	31	31	436	437	-11	10	11	11	12	12	13	13
-7	48	1314	1314	1482	1482	1311	1311	32	32	215	206	-11	10	11	11	12	12	13	13
-7	50	225	225	274	274	221	221	33	33	1798	1818	-11	10	11	11	12	12	13	13
-7	52	345	345	264	264	283	283	34	34	61	61	-11	10	11	11	12	12	13	13
-7	54	1981	1981	981	981	998	998	35	35	1456	1480	-11	10	11	11	12	12	13	13
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-7	58	187	187	487	487	116	116	37	37	130	128	-11	10	11	11	12	12	13	13
-7	60	348	348	487	487	116	116	38	38	456	458	-11	10	11	11	12	12	13	13
-7	62	850	850	119	119	116	116	39	39	133	132	-11	10	11	11	12	12	13	13
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-7	66	475	475	334	334	260	260	41	41	214	220	-11	10	11	11	12	12	13	13
-7	68	1471	1471	1482	1482	538	538	42	42	256	255	-11	10	11	11	12	12	13	13
-7	70	1314	1314	1482	1482	1311	1311	43	43	229	231	-11	10	11	11	12	12	13	13
-7	72	225	225	274	274	283	283	44	44	1954	1988	-11	10	11	11	12	12	13	13
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-7	108	139	139	187	187	138	138	62	62	199	209	-11	10	11	11	12	12	13	13
-7	110	475	475	334	334	260	260	63	63	419	239	-11	10	11	11	12	12	13	13
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-7	142	1981	1981	981	981	998	998	79	79	1	2	-11	10	11	11	12	12	13	13
-7	144	487	487	119	119	116	116	80	80	1	2	-11</td							

B	L	PO	PC	B	L	PO	PC	B	L	PO	PC	B	L	PO	PC	B	L	PO	PC
-7	7	254	233	8	8	609	617	9	9	109	112	10	10	112	112	11	11	111	111
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-7	12	260	252	14	14	748	703	15	15	461	461	16	16	470	470	17	17	470	470
-7	18	310	286	20	20	360	310	21	21	136	136	22	22	219	219	23	23	219	219
-7	22	286	287	24	24	140	140	25	25	134	134	26	26	121	121	27	27	121	121
-6	10	291	292	11	11	512	512	12	12	536	536	13	13	535	535	14	14	535	535
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-6	19	250	250	20	20	643	1057	21	21	150	150	22	22	150	150	23	23	150	150
-6	22	282	282	24	24	638	638	25	25	461	461	26	26	461	461	27	27	461	461
-6	24	150	150	26	26	471	471	27	27	527	527	28	28	499	499	29	29	499	499
-6	28	527	527	30	30	518	518	31	31	556	556	32	32	532	532	33	33	532	532
-6	32	556	556	34	34	1147	1147	35	35	655	655	36	36	655	655	37	37	655	655
-6	36	655	655	38	38	122	122	39	39	871	871	40	40	871	871	41	41	871	871
-6	40	871	871	42	42	232	232	43	43	94	94	44	44	94	94	45	45	94	94
-6	44	94	94	46	46	986	986	47	47	75	75	48	48	75	75	49	49	75	75
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-6	64	727	727	66	66	147	147	67	67	357	357	68	68	357	357	69	69	357	357
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-6	82	169	169	84	84	279	279	85	85	294	294	86	86	294	294	87	87	294	294

H	L	PO	PC	H	L	PO	PC	H	L	PO	PC	H	L	PO	PC	H	L	PO	PC
-9	21	188	185	-9	22	193	203	-9	24	186	201	-9	26	249	259	-8	27	218	377
-9	20	203	375	-9	23	328	203	-9	25	122	138	-9	27	370	355	-8	28	630	633
-8	19	104	117	-8	21	194	174	-8	23	116	115	-8	25	314	338	-8	27	928	944
-8	18	129	115	-8	20	129	115	-8	22	314	338	-8	24	651	692	-8	26	375	365
-8	17	116	115	-8	19	928	217	-8	21	651	496	-8	23	496	497	-8	25	107	124
-8	16	241	944	-8	18	180	176	-8	20	684	721	-8	22	107	144	-8	24	444	426
-8	15	651	151	-8	17	107	151	-8	19	444	426	-8	21	417	149	-8	23	754	760
-8	14	375	426	-8	16	496	497	-8	18	444	426	-8	20	425	353	-8	22	347	421
-8	13	365	426	-8	15	180	176	-8	17	684	721	-8	19	1245	181	-8	21	115	99
-8	12	375	426	-8	14	107	151	-8	16	107	151	-8	18	149	84	-8	20	25	0
-8	11	124	151	-8	13	144	149	-8	15	124	181	-8	17	115	99	-8	19	754	770
-8	10	151	149	-8	12	149	84	-8	14	149	84	-8	16	425	460	-8	18	10	11
-8	9	99	76	-8	11	99	76	-8	13	181	188	-8	15	1245	181	-8	17	1245	181
-8	8	76	770	-8	10	425	460	-8	12	425	460	-8	14	446	159	-8	16	1245	181
-8	7	770	1261	-8	9	1261	188	-8	11	1261	188	-8	13	1245	181	-8	15	1245	181
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-7	21	181	190	-7	22	413	108	-7	23	167	216	-7	24	167	216	-7	25	167	216
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-7	19	229	952	-7	20	413	108	-7	21	167	216	-7	22	167	216	-7	23	167	216
-7	18	952	678	-7	19	413	108	-7	20	167	216	-7	21	167	216	-7	22	167	216
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-7	13	384	746	-7	14	413	108	-7	15	167	216	-7	16	167	216	-7	17	167	216
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-7	7	354	532	-7	8	413	108	-7	9	167	216	-7	10	167	216	-7	11	167	216
-7	6	532	1271	-7	7	413	108	-7	8	167	216	-7	9	167	216	-7	10	167	216
-7	5	1271	1011	-7	6	413	108	-7	7	167	216	-7	8	167	216	-7	9	167	216
-7	4	1011	547	-7	5	413	108	-7	6	167	216	-7	7	167	216	-7	8	167	216
-7	3	547	318	-7	4	413	108	-7	5	167	216	-7	6	167	216	-7	7	167	216
-7	2	318	192	-7	3	413	108	-7	4	167	216	-7	5	167	216	-7	6	167	216
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S	L	PO	PC	H	L	PO	PC	H	L	PO	PC	S	L	PO	PC
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-10	19	281	283	-6	6	614	634	-2	2	309	323	6	471	479	479
-10	20	590	607	-6	7	188	174	-2	2	136	113	6	461	489	74
-10	24	151	170	-6	8	804	822	-2	2	834	533	9	97	159	159
-10	25	145	123	-6	9	770	770	-2	2	293	995	10	187	129	129
-10	26	364	348	-6	10	453	448	-2	2	108	837	11	281	271	271
-10	27	158	169	-6	11	419	436	-2	2	204	824	12	327	308	308
-10	28	102	110	-6	12	93	310	-2	2	251	113	1	752	747	747
-10	29	634	633	-6	13	536	527	-2	2	181	487	1	191	198	198
-10	30	414	386	-6	14	298	301	-2	2	487	859	2	613	616	616
-10	31	304	307	-6	15	370	372	-2	2	260	235	3	218	214	214
-10	32	406	413	-6	16	191	209	-2	2	1567	1556	4	344	326	326
-10	33	440	428	-6	17	149	163	-2	2	556	4962	5	151	144	144
-10	34	496	502	-6	18	499	490	-2	2	401	488	6	118	122	122
-10	35	578	584	-6	19	211	228	-2	2	140	144	7	407	358	358
-10	36	200	214	-6	20	237	1031	-2	2	664	441	8	221	217	217
-10	37	161	122	-6	21	0	602	-2	2	1219	292	9	627	623	623
-10	38	371	398	-6	22	1	829	-2	2	254	354	10	245	253	253
-10	39	138	127	-6	23	237	237	-2	2	354	354	11	270	258	258
-10	40	527	517	-6	24	55	585	-2	2	1580	1580	12	113	108	108
-10	41	150	153	-6	25	6	813	-2	2	566	566	13	133	87	87
-10	42	317	322	-6	26	7	84	-2	2	429	429	14	203	537	537
-10	43	148	153	-6	27	9	990	-2	2	183	183	15	238	219	219
-10	44	384	387	-6	28	99	977	-2	2	292	292	16	463	306	306
-10	45	128	138	-6	29	10	159	-2	2	268	268	17	423	423	423
-10	46	152	153	-6	30	306	301	-2	2	362	362	18	368	346	346
-10	47	523	519	-6	31	11	331	-2	2	475	575	19	368	321	321
-10	48	300	307	-6	32	12	624	-2	2	562	141	20	255	230	230
-10	49	697	705	-6	33	13	521	-2	2	151	831	21	133	113	113
-10	50	164	152	-6	34	14	369	-2	2	443	219	22	167	149	149
-10	51	132	130	-6	35	15	379	-2	2	80	85	23	113	95	95
-10	52	139	156	-6	36	16	288	-2	2	130	125	24	126	108	108
-10	53	374	387	-6	37	17	261	-2	2	443	417	25	156	321	321
-10	54	642	663	-6	38	18	241	-2	2	888	862	26	116	254	254
-10	55	315	342	-6	39	19	267	-2	2	254	248	27	116	103	103
-10	56	422	408	-6	40	20	247	-2	2	135	126	28	120	91	91
-10	57	102	83	-4	41	21	200	-2	2	206	192	29	113	112	112
-10	58	379	306	-4	42	22	241	-2	2	167	162	30	113	108	108
-10	59	318	392	-4	43	23	234	-2	2	839	299	31	113	112	112
-10	60	660	663	-4	44	24	220	-2	2	140	131	32	113	108	108
-10	61	198	195	-4	45	25	1170	-2	2	282	230	33	113	112	112
-10	62	277	260	-4	46	26	448	-2	2	553	595	34	113	112	112
-10	63	237	219	-4	47	27	817	-2	2	353	370	35	113	112	112
-10	64	276	309	-4	48	28	522	-2	2	282	270	36	113	112	112
-10	65	167	151	-4	49	29	547	-2	2	575	441	37	113	112	112
-10	66	315	305	-4	50	30	176	-2	2	977	964	38	113	112	112
-10	67	695	716	-4	51	31	152	-2	2	553	941	39	113	112	112
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-10	69	344	330	-4	53	33	1571	-2	2	271	232	41	113	112	112
-10	70	90	56	-4	54	34	962	-2	2	425	441	42	113	112	112
-10	71	321	324	-4	55	35	908	-2	2	168	164	43	113	112	112
-10	72	345	502	-4	56	36	193	-2	2	345	345	44	113	112	112
-10	73	502	213	-4	57	37	105	-2	2	743	743	45	113	112	112
-10	74	191	523	-4	58	38	1571	-2	2	572	578	46	113	112	112
-10	75	695	716	-4	59	39	923	-2	2	734	728	47	113	112	112
-10	76	344	330	-4	60	40	191	-2	2	204	187	48	113	112	112
-10	77	90	56	-4	61	41	353	-2	2	471	459	49	113	112	112
-10	78	321	324	-4	62	42	523	-2	2	821	776	51	113	112	112
-10	79	502	213	-4	63	43	245	-2	2	449	455	52	113	112	112
-10	80	191	523	-4	64	44	1373	-2	2	363	349	53	113	112	112
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-10	84	321	324	-4	68	48	387	-2	2	821	776	57	113	112	112
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-10	90	321	324	-4	74	54	437	-2	2	821	776	63	113	112	112
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B	L	P0	PC	B	L	P0	PC	B	L	P0	PC	B	L	P0	PC	B	L	P0	PC
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9	5	193	190	-9	18	282	277	-6	23	534	534	-2	7	112	582	-2	12	212	113
9	6	K	****	-9	19	294	295	-6	24	113	113	-2	6	556	357	-2	12	212	113
9	7	275	249	-9	20	294	295	-6	25	148	148	-2	5	423	232	-2	12	212	113
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9	9	156	171	-11	17	223	230	-7	23	263	234	-7	22	215	335	-3	3	33	116	116	413	413	
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R	P0	PC	B	L	P0	PC																
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12	270	202	-8	19	405	172	-8	17	294	379	-1	15	978	978	-1	16	978	978	-1	16	60	60
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-12	17	137	138	-6	10	620	614	-1	10	175	210	-10	16	340	157
-12	19	286	274	-6	11	206	145	-1	11	279	306	-9	19	157	243
-11	9	246	240	-6	12	242	232	-1	12	192	144	-9	21	257	333
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-11	12	211	220	-6	14	469	442	-1	14	546	521	-9	25	122	185
-11	14	115	223	-6	15	703	236	-1	15	454	443	-9	27	418	273
-11	15	282	281	-6	16	126	133	-1	16	386	415	-9	29	187	184
-11	17	203	228	-6	17	240	227	-1	17	360	354	-9	31	127	133
-11	18	155	158	-6	18	443	426	-1	18	149	183	-9	33	415	393
-11	19	234	231	-6	19	518	533	-1	19	527	507	-9	35	171	171
-10	4	183	158	-6	20	336	326	-1	20	169	184	-8	37	180	85
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-4	6	411	400	6	7	220	178	-7	10	196	289	-1	1	524	227
-4	7	112	74	7	9	172	194	-7	11	131	147	-1	1	226	318
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-4	14	233	245	14	13	264	256	-6	3	432	104	0	0	70	70
-4	15	359	364	15	13	175	131	-6	4	184	442	0	0	178	178
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-7	17	272	275	344	216	185	185	-1	357	270	386	-2	11	139	139
-7	18	179	160	155	372	366	366	-1	302	156	270	-1	11	668	644
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-4	19	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	0	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	1	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	2	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	3	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	4	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	5	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	6	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	7	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	8	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	9	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	10	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	11	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	12	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	13	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	14	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	15	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	16	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	17	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	18	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	19	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	0	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	1	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	2	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	3	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	4	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	5	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	6	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	7	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	8	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	9	115	118	157	157	357	357	-1	194	194	194	-1	12	122	106
-4	10	115	118	157											

B	L	PO	PC	B	L	PO	PC	B	L	PO	PC	B	L	PO	PC
1	7	261	258	-4	5	116	150	-1	1	468	468	-2	6	120	76
2	11	298	323	-4	7	276	272	-1	7	314	306	-2	7	346	309
3	3	236	197	-4	11	137	123	-1	9	229	240	-1	151	149	313
4	3	161	165	-4	2	275	281	0	1	263	267	-1	321	313	313
5	3	185	172	-4	3	125	126	1	7	362	373	-1	125	136	200
6		****	****	-4	4	357	357	3	5	265	280	0	180	180	246
7	K	= 18	****	-4	5	143	116	1	1	142	131	0	218	218	243
8	7	186	198	-4	5	153	153	3	1	19	****	2	24	28	28
9	9	302	283	-4	9	164	150	****	7	154	133	1	37	35	335
10	3	130	127	-4	11	333	346	-4	1	311	306	1	148	161	233
11	5	221	209	-4	11	230	214	-3	2	120	119	1	23	23	235
12	7	205	203	-4	2	338	339	-3	7	268	271	2			
13	9	205	165	-4	2	136	160	-3	1	167	168	2			
14	11	245	149	-4	3	173	178	-2	3	168	178	2			
15	3	206	234	-4	9	123	103	-2	5	207	225	2			
16	3	333	202	-4	9	341	315	-2				2			

TABLE VI

Interatomic Distances (\AA)

Ru-B10	2.023(5)	B9-H9	1.10(6)
Ru-C2	2.097(4)	B9-B10	1.795(7)
Ru-C29	2.167(4)	B10-H10	1.06(6)
Ru-C3	2.185(4)	C2...C3	2.692(6)
Ru-C28	2.191(4)	B7...B9	2.826
Ru-B9	2.340(5)	B10...C2	2.833
Ru-P	2.418(1)	B10...C3	2.806
Ru-B7	2.466(5)	B10...B4	2.951
Ru-B1	2.488(5)	B10...B5	2.956
P-C21	1.826(4)	C21-C22	1.398(6)
P-C11	1.824	C21-C26	1.405(6)
P-C31	1.828	C22-H22	0.96(6)
		C22-C23	1.390(6)
B1-H1	1.03(6)	C23-H23	0.92(6)
B1-C3	1.609(6)	C23-C23	1.381(7)
B1-C2	1.635(6)	C24-H24	0.89(6)
B1-B4	1.814(7)	C24-C25	1.380(7)
B1-B5	1.820(7)	C25-H25	0.93(6)
		C25-C26	1.396(6)
C2-Me1	1.527	C26-C27	1.498(6)
C2-B9	1.584(6)	B4-H4	1.06(6)
C2-B1	1.635(6)	B4-B5	1.743(7)
C2-B5	1.685(6)	B4-B3	1.790(8)
C3-Me2	1.519	B4-B7	1.800(8)
C3-B7	1.578(7)	B5-H5	1.11(6)
C3-B1	1.609(6)	B5-B9	1.80(7)
C3-B4	1.688(6)	B5-B3	1.808(7)
B4-H4	1.06(6)	B7-H7	1.10(6)
B4-B5	1.743(7)	B7-B8	1.797(7)
B4-B3	1.790(8)	B7-B10	1.807(7)
B4-B7	1.800(8)	B8-H3	1.09(6)
		B8-B10	1.782(7)
		B8-B9	1.814(7)

TABLE VII

Average Bond Lengths

<u>Atoms</u>	<u>No.</u>	<u>Range, (A)</u>	<u>Av.^a(A)</u>
Ru-C	4	2.097(4)-2.191(4)	2.16(4)
Ru-B	4	2.023(5)-2.488(5)	2.33(22)
C-C ^b	6	1.380(7)-1.405(6)	1.392(10)
B-B	12	1.743-1.820	1.80(2)
C-B	8	1.584(6)-1.688(6)	1.63(10)
B-H	7	1.06(6)-1.11(6)	1.08(2)
C-H	9	0.89(6)-1.02(6)	0.95(5)

$$^a \sigma = [\sum_{i=1}^N (X_i - \bar{X})^2 / (N-1)]^{1/2}$$

^b C-C for distances within phenyl ring of o-allylphenyl group

TABLE VIII

Interatomic Angles (deg)

B10-Ru-C2	86.9(2)	C3-B1-C2	112.1(4)
B10-Ru-C29	109.5(2)	C3-B1-B4	58.7(3)
B10-Ru-C3	83.6(2)	C3-B1-B5	105.8(4)
B10-Ru-C28	82.4(2)	C3-B1-Ru	60.0(2)
B10-Ru-B9	47.9(2)	C2-B1-B4	105.8(3)
B10-Ru-P	126.7(1)	C2-B1-B5	58.1(3)
B10-Ru-B7	46.2(2)	C2-B1-Ru	56.7(2)
B10-Ru-B1	94.5(2)	B4-B1-B5	57.3(3)
C2-Ru-C29	90.2(2)	B4-B1-Ru	95.5(3)
C2-Ru-C28	115.0(2)	B5-B1-Ru	93.3(3)
C2-Ru-C3	77.9(2)		
C2-Ru-B9	41.4(2)	B9-C2-Me1	120.9
C2-Ru-P	144.2(1)	B9-C2-B1	115.5(3)
C2-Ru-B7	88.7(2)	B9-C2-B5	66.9(3)
C2-Ru-B1	40.7(2)	B9-C2-Ru	77.5(2)
C29-Ru-C3	162.0(2)	B1-C2-Me1	120.2
C29-Ru-C28	37.6(2)	B1-C2-B5	66.4(3)
C29-Ru-B9	91.4(2)	B1-C2-Ru	82.6(2)
C29-Ru-P	89.3(1)	B5-C2-Me1	120.0
C29-Ru-B7	155.7(2)	B5-C2-Ru	113.3(3)
C29-Ru-B1	124.5(2)	Ru-C2-Me1	126.7
C3-Ru-C28	160.3(2)		
C3-Ru-B9	88.5(2)	B7-C3-Me2	119.2
C3-Ru-P	92.5(1)	B7-C3-B1	117.2(4)
C3-Ru-B7	39.1(2)	B7-C3-B4	66.8(3)
C3-Ru-B1	39.6(2)	B7-C3-Ru	80.1(2)
C28-Ru-B9	92.3(2)	B1-C3-Me2	118.7
C28-Ru-P	84.9(1)	B1-C3-B4	66.7(3)
C28-Ru-B7	123.1(2)	B1-C3-Ru	80.4(2)
C28-Ru-B1	155.6(2)	B4-C3-Me2	117.9
B9-Ru-P	174.4(1)	B4-C3-Ru	111.7(3)
B9-Ru-B7	72.0(2)	Ru-C3-Me2	130.4
B9-Ru-B1	68.6(2)		
P-Ru-B7	105.5(1)	H4-B4-C3	123(3)
P-Ru-B1	115.4(1)	H4-B4-B5	124(3)
B7-Ru-B1	66.6(2)	H4-B4-B8	123(3)
		H4-B4-B7	122(3)
Ru-P-C11	107.4	H4-B4-B1	128(3)
Ru-P-C21	113.8(1)	C3-B4-B5	105.9(3)
Ru-P-C31	101.2	C3-B4-B8	102.5(3)
C11-P-C21	103.4	C3-B4-B7	53.7(3)
C11-P-C31	108.3	C3-B4-B1	54.6(3)
C21-P-C31	101.2	B5-B4-B8	61.6(3)
		B5-B4-B7	107.9(4)
H1-B1-C3	120(3)	B5-B4-B1	61.5(3)
H1-B1-C2	119(3)	B8-B4-B7	60.1(3)
H1-B1-B4	127(3)	B8-B4-B1	104.9(3)
H1-B1-B5	125(3)	B7-B4-B1	97.7(3)
H1-B1-Ru	132(3)		

Table VIII (cont'd)

H5-B5-C2	117(3)	B10-B9-B5	110.4(4)
H5-B5-B4	128(3)	B10-B9-B8	59.2(3)
H5-B5-B9	121(3)	B10-B9-Ru	56.8(2)
H5-B5-B8	129(3)	B5-B9-B8	60.0(3)
H5-B5-B1	125(3)	B5-B9-Ru	98.9(3)
C2-B5-B4	106.8(3)	B8-B9-Ru	94.3(3)
C2-B5-B9	53.9(3)		
C2-B5-B8	103.4(3)	H10-B10-B8	120(3)
C2-B5-B1	55.5(2)	H10-B10-B9	118(3)
B4-B5-B9	107.1(4)	H10-B10-B7	132(3)
B4-B5-B8	60.5(3)	H10-B10-Ru	132(3)
B4-B5-B1	61.2(3)	B8-B10-B9	60.9(3)
B9-B5-B8	60.3(3)	B8-B10-B7	60.1(3)
B9-B5-B1	97.4(3)	B8-B10-Ru	107.2(3)
B8-B5-B1	103.9(3)	B9-B10-B7	103.3(3)
		B9-B10-Ru	75.3(2)
H7-B7-C3	122(3)	B7-B10-Ru	79.9(3)
H7-B7-B8	124(3)		
H7-B7-B4	124(3)	C22-C21-C26	119.7(4)
H7-B7-B10	117(3)	C22-C21-P	122.3(3)
H7-B7-Ru	136(3)	C26-C21-P	118.0(3)
C3-B7-B8	106.8(4)		
C3-B7-B4	59.5(3)	H22-C22-C23	122(4)
C3-B7-B10	111.8(3)	H22-C22-C21	117(4)
C3-B7-Ru	60.8(2)	C21-C22-C23	120.6(4)
B8-B7-B4	59.7(3)		
B8-B7-B10	59.3(3)	H23-C23-C24	117(4)
B8-B7-Ru	90.6(3)	H23-C23-C22	123(4)
B4-B7-B10	109.8(4)	C24-C23-C22	119.8(4)
B4-B7-Ru	96.7(3)		
B10-B7-Ru	53.9(2)	H24-C24-C25	117(4)
		H24-C24-C23	122(4)
		C25-C24-C23	120.0(4)
H8-B8-B10	117(3)		
H8-B8-B4	121(3)	H272-C27-H271	108(5)
H8-B8-B7	122(3)	H272-C27-C26	110(4)
H8-B8-B5	124(3)	H272-C27-C28	108(4)
H8-B8-B9	127(3)	H271-C27-C26	108(3)
B10-B8-B4	111.4(4)	H271-C27-C28	109(3)
B10-B8-B7	60.6(3)	C26-C27-C28	113.8(4)
B10-B8-E5	110.8(3)		
B10-B8-B9	59.9(3)	H25-C25-C24	123(4)
B4-B8-B7	60.2(3)	H25-C25-C26	115(4)
B4-B8-B5	57.9(3)	C24-C25-C26	121.5(4)
B4-B8-B9	104.7(3)		
B7-B8-B5	105.2(4)	C25-C26-C21	118.5(4)
B7-B8-B9	103.0(3)	C25-C26-C27	120.5(4)
B5-B8-B9	59.7(3)	C21-C26-C27	121.0(4)
H9-B9-C2	123(3)	H28-C28-C29	110(3)
H9-B9-B10	110(3)	H28-C28-C27	115(3)
H9-B9-B5	131(3)	H28-C28-Ru	107(3)
H9-B9-B8	126(3)	C29-C28-C27	125.2(4)
H9-B9-Ru	126(3)	C29-C28-Ru	70.3(2)
C2-B9-B10	113.8(3)	C27-C28-Ru	120.5(3)
C2-B9-B5	59.2(3)		
C2-B9-B8	107.5(4)		
C2-B9-Ru	61.1(2)		

Table VIII (cont'd)

H292-C29-H291	124(6)
H292-C29-C28	114(6)
H292-C29-Ru	104(4)
H291-C29-C28	119(4)
H291-C29-Ru	109(4)
C28-C29-Ru	72.1(2)

TABLE IX

Selected Least-Squares Planes and Interplanar Angles

Atom	a) Distances of Atoms from Least-Squares Planes ^a , ($\text{\AA} \times 10^3$)						
	Plane I ^b	Plane II	Plane III	Plane IV	Plane V	Plane VI	Plane VII ^c
Ru	-1595	-1103	-1776		-2077	-2088	21*
P	-3304	-976	-3464	-48	-2232	-2026	-1483
B(1)	616	864	-1596				-14*
C(2)	6*	1*	-1345		-2138	-2581	1338
C(3)	-6*	-1*	-1351		-4220	-4267	-1353
B(4)	1468	2*	0*				-831
B(5)	1466	-2*	0*				910
B(7)	6*	1424	0*		-4126	-3881	-1423
B(8)	955	-1564	1003				20*
B(9)	-6*	-1439	0*		-1925	-2092	1399
B(10)	-820	-2466	221				-27*
C(21)				2*			-764
C(22)				-1*			-894
C(23)				4*			-357
C(24)				-3*			299
C(25)				-1*			433
C(26)				3*	329	722	-86
C(27)				70	53*	548	129
C(28)	-3255				-184*	19*	939
C(29)	-2968				59*	-80*	1642
H(28)					72*	322	1430
H(291)					239	32*	1538
H(292)					305	29*	2400

b) Interplanar Angles, Deg

[B(7), B(9), B(10)]-[Plane I]	47.2°
[B(1), C(2), C(3)]-[Plane I] ^d	42.7°
[B(7), B(8), B(9)]-[Plane I]	58.2°

^aAtoms used to define the least-squares planes are indicated by asterisks. ^bPlanes are defined as $Ax + By + Cz = D$, where x, y, z are orthogonal coordinates (in Angströms) and the axes parallel a , b , and c^* . Plane I $-0.8734x + 0.4115y + 0.2606z = 7.117$
 Plane II $-0.0396x + 0.9958y - 0.08272 = 4.5789$
 Plane III $-0.7658x - 0.5598y + 0.3164z = 3.5757$

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ABSTRACT

Reactions of [hyper-closo-2-R¹-3-R²-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₇](I) with (*o*-styryl)diphenylphosphine (R^{1,2}=H,CH₃; R¹=H,R²=Ph), (*o*-allylphenyl)diphenylphosphine(R^{1,2}=H,CH₃) and Ph_{3-n}P(CH₂CH₂CH=CH₂)_n(n=1,2; R^{1,2}=CH₃) afforded the 16e⁻ ruthenacarborane complexes [hyper-closo-RuL(C₂B₇H₇R¹R²)] (IIa-g), in which the alkenyl phosphine (L) functions as a bidentate ligand. The crystal structure of [2,3-(CH₃)₂-6-(CH₂=CHCH₂C₆H₄Ph₂P)-6,2,3-RuC₂B₇H₇](IId) was determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group P2₁/c with a=11.740(3) Å, b=15.185(5) Å, c=21.748(7) Å, β=137.43(2)⁰ and Z=4. Refinement of 4168 independent reflections with I>3σ(I) led to a final value of R=4.0%. The structure of this complex may best be described in terms of a C₂B₇ fragment of arachno-geometry which occupies nine vertices of an eleven-vertex octadecahedron with a ruthenium atom in a "non-vertex" position and within bonding distance of six atoms in the open face. The observed distortion from the common ten-vertex bicapped square antiprismatic structure is thought to be a result of the perturbation of the polyhedral skeletal bonding induced by the sixteen-electron Ru^{II} center. Reaction of (IIb) with carbon monoxide displaced the coordinated alkenyl side-chain to yield the 18e⁻ Ru^{II} complex [closo-6,6-(CO)₂-6-L-6,2,3-RuC₂B₇H₉](IIIa){L= (*o*-allylphenyl)-diphenylphosphine}.

Reactions of Ph_{3-n}P(CH₂CH₂CH=CH₂)_n(n=1,2) with [hyper-closo-6,6-(PPh₃)₂-6,2,3-RuC₂B₇H₉] produced the fluxional complexes [closo-6,6-L₂-6,2,3-RuC₂B₇H₉](IVa-b) which exhibit butenyl side-chain exchange and undergo closo-hyper-closo equilibria as evidenced by variable temperature multinuclear FTNMR spectroscopy. The reactions of (IVa-b) with carbon monoxide are also discussed.

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